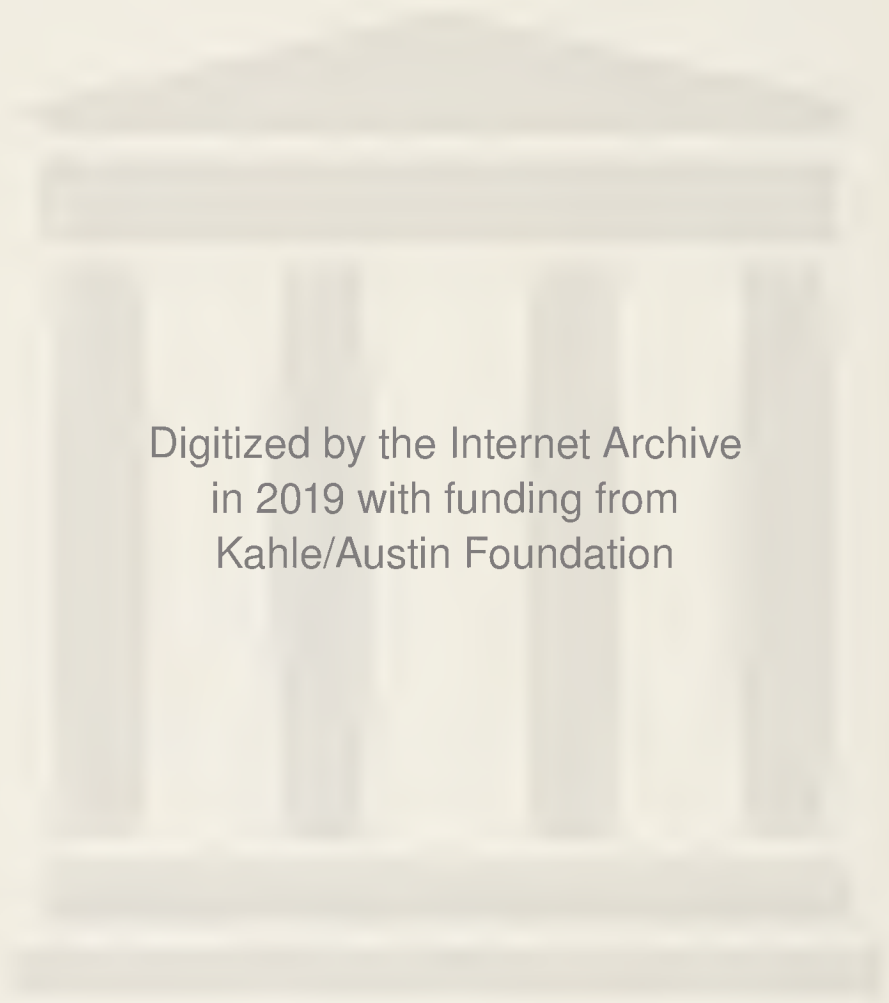


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ADVANCES IN CHEMICAL PHYSICS
VOLUME VI

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ADVANCES IN CHEMICAL PHYSICS

Edited by I. PRIGOGINE

University of Brussels, Brussels, Belgium

VOLUME VI

INTERSCIENCE PUBLISHERS

a division of John Wiley & Sons Ltd., London - New York - Sydney

FIRST PUBLISHED 1964

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PRINTED IN GREAT BRITAIN BY THE
FITMAN PRESS, BATH AND LONDON

INTRODUCTION

In the last decades, chemical physics has attracted an ever increasing amount of interest. The variety of problems, such as those of chemical kinetics, molecular physics, molecular spectroscopy, transport processes, thermodynamics, the study of the state of matter, and the variety of experimental methods used, makes the great development of this field understandable. But the consequence of this breadth of subject matter has been the scattering of the relevant literature in a great number of publications.

Despite this variety and the implicit difficulty of exactly defining the topic of chemical physics, there are a certain number of basic problems that concern the properties of individual molecules and atoms as well as the behavior of statistical ensembles of molecules and atoms. This new series is devoted to this group of problems which are characteristic of modern chemical physics.

As a consequence of the enormous growth in the amount of information to be transmitted, the original papers, as published in the leading scientific journals, have of necessity been made as short as is compatible with a minimum of scientific clarity. They have, therefore, become increasingly difficult to follow for anyone who is not an expert in this specific field. In order to alleviate this situation, numerous publications have recently appeared which are devoted to review articles and which contain a more or less critical survey of the literature in a specific field.

An alternative way to improve the situation, however, is to ask an expert to write a comprehensive article in which he explains his view on a subject freely and without limitation of space. The emphasis in this case would be on the personal ideas of the author. This is the approach that has been attempted in this new series. We hope that as a consequence of this approach, the series may become especially stimulating for new research.

Finally, we hope that the style of this series will develop into something more personal and less academic than what has become

the standard scientific style. Such a hope, however, is not likely to be completely realized until a certain degree of maturity has been attained—a process which normally requires a few years.

At present, we intend to publish one volume a year, but this schedule may be revised in the future.

In order to proceed to a more effective coverage of the different aspects of chemical physics, it has seemed appropriate to form an editorial board. I want to express to them my thanks for their cooperation.

I. PRIGOGINE

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TOWARD AN ANALYTIC THEORY OF CHEMICAL REACTIONS

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I. INTRODUCTION

The main purpose of an analytic approach to the theory of chemical reactions is to furnish a detailed understanding of the elements involved, rather than to provide a quick comparison with experimentally determined macroscopic rates. It is not essential that the particular divisions made in this review be followed in constructing an analytic theory, but some such organization of the problem as presented here will be required. Within the current framework of physical theory it seems natural to consider in sequence the following four steps: identification and characterization of species; interaction of species; collision dynamics; and many-particle dynamics.

Even with the discussion limited largely to isoelectronic bimolecular gaseous reactions, it will be noted that the present status of each of the four elements leaves much to be desired. It is hoped that this review will point up some of the many deficiencies and stimulate research in each of the areas.

II. IDENTIFICATION AND CHARACTERIZATION OF SPECIES

Under certain conditions molecules will react chemically. By this we mean that the molecular species present after collision are different from those prior to collision. The atoms are the same before and after collision, but their configuration in relation to one another is altered so that different molecules are produced. Any kineticist feels he is able to distinguish between reactants and products, and for many practical purposes he can. It is only when an attempt is made to define the species carefully that some confusion occurs. Although this problem is usually ignored in chemical kinetics calculations, it becomes more important the higher the energy, and some attention at least should be given to possible errors in definition, particularly at higher temperatures. In Section II-A we indicate the difficulties involved and some of the theoretical approaches which have been taken.

Presuming some technique for the identification of species, we must then characterize the separated species before and after reaction. In a sense, the isolated species represent boundary conditions or end points of an examination of the total problem,

and it is well that we pay particular attention to them before considering the interaction of species in Section III. Thus, in Section II-B (1) we discuss the Born–Oppenheimer approximation, which provides a sufficient characterization in many instances. In Section II-B (2) we give a brief treatment of the more general Born–Oppenheimer separation.

A. Species Identification*

We first introduce the time-dependent Schrödinger equation (e.g., Reference 88),

$$i\hbar(\partial\Psi/\partial t) = H\Psi \quad (1)$$

which forms the basis of our analysis of the microscopic reacting system (microsystem) as presented in Sections II–IV. The total Hamiltonian H may be represented by

$$H = H_u + V \quad (2)$$

where we regard H_u as the Hamiltonian of unperturbed (isolated) reactants or products, and V as the interaction.

Even if there is no stationary solution for Eq. (1), $\Psi(t)$ may still be expanded in terms of stationary orthonormal wave functions ψ_j , which are solutions of the equation

$$H_u\psi_j = W_j\psi_j \quad (3)$$

The expansion of Ψ is given as

$$\Psi(t) = \sum_j a_j(t) \psi_j e^{-iW_j t/\hbar} \quad (4)$$

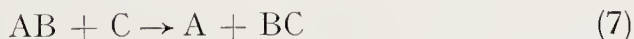
where $a_j(t)$ are coefficients that depend on the time and, of course, implicitly on V . In Eq. (4) the summation sign includes an integration over continuous states. We may also write Eq. (4) as

$$\Psi(t) = \sum_j a_j(t) \Psi_j \quad (5)$$

where

$$\Psi_j = \psi_j e^{-iW_j t/\hbar} \quad (6)$$

Suppose now, that there is a reaction of the type



* Some of the discussion in this section arose from conversations in 1950 with Dr. John K. Bragg.

it would be well to know when we have $AB + C$ and when we have $A + BC$. Two different bases for criteria are usually taken for such questions. If the basis of configuration space is chosen, we would consider that we have the molecule AB when the atoms A and B are within a certain distance of each other. Or if the criterion is based on energy, we would say that the molecule AB exists if the energy in the bond is less than a fixed energy above which we deem the atoms separated.

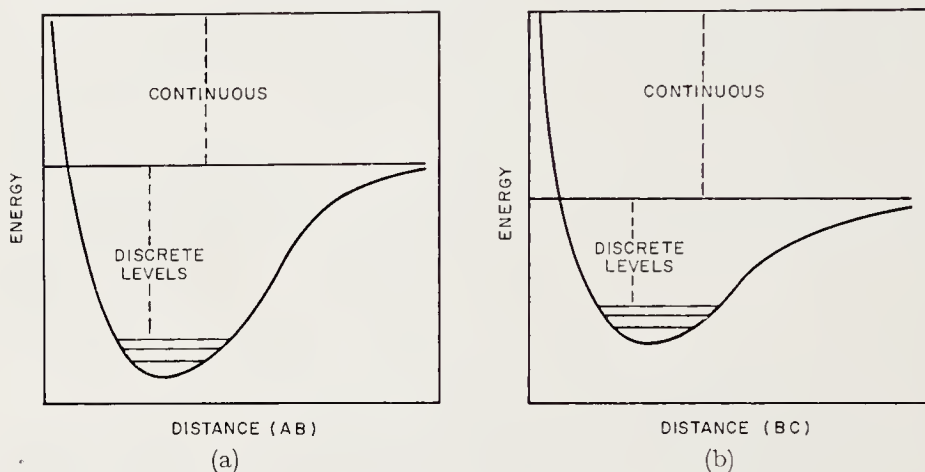


Fig. 1. (a) Energy levels for $\psi_j^{(i)}$, i.e., $AB(+C)$. (b) Energy levels for $\psi_j^{(f)}$, i.e., $BC(+A)$.

The total wave function Ψ for a reaction such as that expressed in Eq. (7) may be expanded in a complete set of initial-state eigenfunctions $\Psi_j^{(i)}$ or in a complete set of final-state eigenfunctions $\Psi_j^{(f)}$ (see Fig. 1, where the energy levels related to these eigenfunctions are depicted). Thus we can have

$$\Psi = \sum_j a_j^{(i)}(t) \Psi_j^{(i)} \quad (8a)$$

or

$$\Psi = \sum_j a_j^{(f)}(t) \Psi_j^{(f)} \quad (8b)$$

where the Hamiltonians associated with $\psi_j^{(f)}$ and $\psi_j^{(i)}$ do not in general commute, and $\psi_j^{(i)}$ is not orthogonal to $\psi_j^{(f)}$.

With both sets complete, it would be possible to describe mathematically all physical processes as occurring within either of the sets. Neither procedure, however, yields a treatment with sufficient physical significance for ordinary interpretation by the

chemist. For example, if we were to choose the complete set of initial-state eigenfunctions as a basis, there would indeed be transitions from "observable" discrete initial states to other "observable" discrete initial states, which we would interpret as "collisions without reaction." But there would also be transitions from "observable" initial states to "continuous" initial states, which we deem "nonobservable" as initial reactants and refer to physically as "observable" products of "collisions with reaction".

It therefore seems that what is required for adequate physical representation is a mixture of the two sets. To this end Langer⁵⁶ wrote

$$\Psi \cong \sum_j^{s \doteq 0} a_j^{(i)}(t) \Psi_j^{(i)} + \sum_j^{s \neq 0} a_j^{(f)}(t) \Psi_j^{(f)} \quad (9)$$

where the summations are only over those $\Psi_j^{(i)}$ and $\Psi_j^{(f)}$ for which

$$s = \int \psi_j^{(i)*} \psi_j^{(f)} d\tau \doteq 0 \quad (10)$$

If the energy in either the initial or final state is sufficiently high, then we have $s \neq 0$, and we are thus imposing an approximate energy criterion for species identification.

We may easily derive from Eq. (9) mathematical statements of the approximate equivalence, physically implied above, between continuous initial states and discrete final states, and vice versa. Rewriting Eq. (8a) in the form

$$\Psi = \sum_j^{s \doteq 0} a_j^{(i)}(t) \Psi_j^{(i)} + \sum_j^{s \neq 0} a_j^{(i)}(t) \Psi_j^{(i)} \quad (11)$$

and combining it with Eq. (9), we have

$$\sum_j^{s \doteq 0} a_j^{(f)}(t) \Psi_j^{(f)} \cong \sum_j^{s \neq 0} a_j^{(i)}(t) \Psi_j^{(i)} \quad (12a)$$

Similarly, we may also obtain

$$\sum_j^{s \doteq 0} a_j^{(i)}(t) \Psi_j^{(i)} \cong \sum_j^{s \neq 0} a_j^{(f)}(t) \Psi_j^{(f)} \quad (12b)$$

Equations (12), which have arisen because of the nonorthogonality of $\psi_j^{(f)}$ to $\psi_j^{(i)}$, demonstrate the inherent difficulties of definition by the energy method in that one is not able to distinguish absolutely between the final and initial states. Because of this

nonorthogonality we cannot hope to obtain exact criteria based on energy cut-offs.*

Criteria based on configuration considerations can be set up so as to avoid such errors of distinguishability. For example, referring to Eq. (5) with δ_1 as the distance between A and B, and δ_2 as the distance between B and C, we can set up the following configuration criterion (see Fig. 2). Suppose $\delta_1 \leq \delta_1^{(0)}$ and

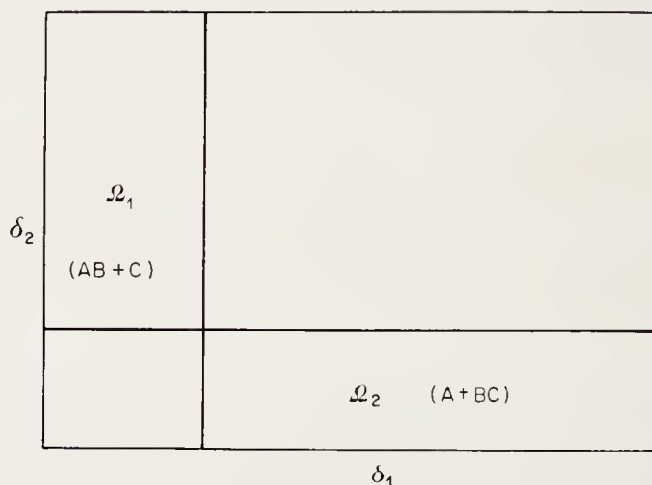


Fig. 2. Configuration criterion.

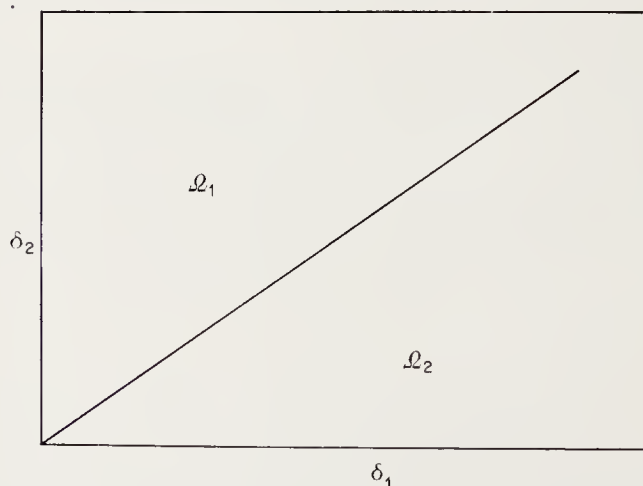


Fig. 3. Another configuration criterion.

* When the initial and final states can be described adequately in terms of one complete set, as in the dissociation reaction $AB \rightarrow A + B$, an arbitrary but exact energy criterion is possible.

$\delta_2 \geq \delta_2^{(0)}$ together define a region Ω_1 , where we have $AB + C$. Similarly, $\delta_2 \leq \delta_2^{(0)}$ and $\delta_1 \geq \delta_1^{(0)}$ define a region Ω_2 of $A + BC$. The regions $(\delta_1 > \delta_1^{(0)}; \delta_2 > \delta_2^{(0)})$ and $(\delta_1 < \delta_1^{(0)}; \delta_2 < \delta_2^{(0)})$ do not count as observable products or reactants. When we omit these regions, however, we have introduced an incompleteness. Although this can be avoided by defining Ω_1 and Ω_2 as shown in Fig. 3, we should understand that with either configuration criterion we would be including as a "bound" molecule AB circumstances when A is colliding with B at great speed and is not really bound to B . For some calculations, therefore, a criterion based on configuration would be misleading.

Still another suggestion is to combine criteria by writing that the probability the system is "observable" as $AB + C$ is

$$\sum_{s \doteq 0}^s |a_j^{(i)}(t)|^2 \int_{\Omega_1} |\psi_j^{(i)}|^2 d\tau$$

and that

$$\sum_{s \doteq 0}^s |a_j^{(f)}(t)|^2 \int_{\Omega_2} |\psi_j^{(f)}|^2 d\tau$$

is the "observability" as $A + BC$. This energy-configuration criterion doubly ensures that we have $AB + C$ or $A + BC$ from configuration and energy viewpoints, but again introduces some indistinguishability.

A general discussion of species identification has been given by Golden.³² The approach he adopts is to see how far one can go in creating a theory of chemical kinetics by making general specifications without regard to the particular means (energy, configuration, or what have you). Then, in principle, species-identification schemes may be fed into the general theory to develop a variety of sub-theories. Golden notes that the desiderata for adequate species identification (classification) are reproducibility, distinguishability, and completeness, all of which are present in the elements of Boolean algebra.* He then defines certain projection operators, called species classification operators, which form the minimal elements of the algebra.

* We hope our brief summary here is understandable without a knowledge of the details of Boolean algebra. See, however, Reference 8.

Specifically, suppose we have

$$\Psi_l = \sum_k c_{lk} \Psi'_k \quad (13)$$

where the Ψ'_k belong to a complete orthonormal set, and Ψ_l may itself be a member of another complete orthonormal set. Then, by analogy with three-dimensional geometry, we have

$$\langle \mathcal{P}[\Psi'_k] \rangle \Psi_l = \Psi'_k \int \Psi'_k \star \Psi_l d\tau = c_{lk} \Psi'_k \quad (14)$$

where the projection operator $\langle \mathcal{P}[\Psi'_k] \rangle$ working on the wave function Ψ_l forms the projection of Ψ_l on Ψ'_k , which is $c_{lk} \Psi'_k$. Furthermore, in the language of the projection operator we have

$$\langle \mathcal{P}[\Psi'_k] \rangle_{ll'} = \int \Psi'_k \star \langle \mathcal{P}[\Psi'_k] \rangle \Psi_{l'} d\tau = c_{lk}^\star c_{l'k} \quad (15)$$

Associating the subscript k with species, we can interpret $\langle \mathcal{P}[\Psi'_k] \rangle_{ll}$ as the probability of species k being in the state l .

Finally, if we abbreviate the operators as $\mathcal{P}_k$, the three characteristics would be

$$\text{reproducibility:} \quad \mathcal{P}_k \mathcal{P}_k = (\mathcal{P}_k)^2 = \mathcal{P}_k \quad (16a)$$

$$\text{distinguishability:} \quad \mathcal{P}_k \mathcal{P}_{k'} = \mathcal{P}_{k'} \mathcal{P}_k = 0 \quad (k \neq k') \quad (16b)$$

$$\text{completeness:} \quad \sum_k \mathcal{P}_k = I \quad (16c)$$

where O and I represent null and identity operators respectively. Equation (16) is, of course, only a formal elegant statement of an ideal, and it is quite another matter to choose suitable specific operators so that Eq. (16) is satisfied. For example, a set of operators related to Fig. 3 would satisfy Eq. (16), but this would probably not be as physically meaningful as the approximate energy or energy-configuration criteria. We should then add a fourth requirement, which is suitability, i.e., the criteria must be appropriate to the considerations at hand.

We shall not delve further into species identification, but shall assume that some satisfactory, albeit approximate, scheme is implicit in the following development.

B. Species Characterization

For several reasons it is important to go beyond the mere identification of the reactants and products. The first is that the common theoretical method used to determine the interaction of species is to calculate the electronic energy of the total system and then subtract the electronic energies of the interacting species (Section III), so that we need the electronic energies of the separated particles. A second reason is that integrals of the kind $\int \psi_j^{(i)*} V \psi_k^{(f)} d\tau$ are needed in the computation of transition probabilities from initial to final states (Section IV), and therefore it is necessary to know the wave functions of the initial and final states. Furthermore, one requires a knowledge of the vibrational, rotational, and translational energies of the particles in the event that a statistical distribution over these energies is assumed (Section V).

(1) *Born–Oppenheimer Approximation*¹¹

The method of the original Born–Oppenheimer approximation* involves an expansion about equilibrium positions. Since isolated molecules may be considered to be near equilibrium in many instances, this development is useful in the description of species before or after reaction. The deficiencies in the present approximation are briefly noted in Section II-B (2).

We may regard Eq. (3) as broken up into a number of equations, one for each of the isolated molecules in the reactant or product phase. Equation (17) below is then representative of one of these equations for one molecule with ν nuclei and n electrons:

$$H_u \psi = \left(\frac{-\hbar^2}{2m} \sum_i^n \nabla_i^2 - \sum_\alpha^\nu \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 + \mathcal{V} \right) \psi = W \psi \quad (17)$$

where m_α designates the mass of the α th nucleus, m the mass of the electrons with i as the running index, and the other symbols have their customary meanings.⁸⁸ Before we dismiss the other definitions, however, it may be well to indicate that we mean $\mathcal{V}$, the

* Methodology relating to a perturbation expansion about an equilibrium configuration is referred to as the Born–Oppenheimer approximation; and the separation *per se* of the nuclear and electronic motions is designated as the Born–Oppenheimer separation.

total potential energy, to contain only the usual electrostatic interactions.*

We want to solve Eq. (17). In the Born–Oppenheimer approximation one takes advantage of the large discrepancy in the masses, m_α and m , to set up an expansion scheme and to separate the two primary motions—electronic and nuclear.† Before giving the formal method we will summarize the semiquantitative arguments⁸⁸ for the choice of the expansion parameter as the fourth root of the ratio of the electronic and nuclear masses. For a molecule of approximate linear dimension a , it is easily shown that the electronic energy $E_e = \hbar^2/ma^2$ and that the vibrational energy $E_v \cong (m/m_\alpha)^{1/2}E_e$. A physically meaningful expansion parameter related to distance rather than energy is the ratio of a typical nuclear vibrational displacement to the dimension a . This is likewise easily demonstrated to be approximately $(E_v/E_e)^{1/2} \cong (m/m_\alpha)^{1/4} = \kappa$. In passing, it is also established that the rotational energy $E_r \cong (m/m_\alpha)E_e$. These approximations are corroborated by the formal expansion in κ given below, where the electronic energy is zeroth order in the parameter κ , the vibrational energy is second order, and the rotational energy is fourth order. The first- and third-order energies vanish, but it should be emphasized that the first- and third-order wave functions do not vanish.

For definiteness one can take

$$\kappa = (m/m_0)^{1/4} \quad (18)$$

where m_0 is the mean of m_α . Defining

$$T_N = - \sum_{\alpha=1}^v \frac{\hbar^2}{2m_\alpha} \nabla_\alpha^2 \quad (19a)$$

and

$$T_E = - \frac{\hbar^2}{2m} \sum_{i=1}^n \nabla_i^2 \quad (19b)$$

* For an excellent brief discussion of the general Hamiltonian, including external electric and magnetic field effects, see Reference 40.

† The overall translational and rotational motion of the system can be separated out of the Hamiltonian initially if a proper transformation of coordinates is made (see Section IV-A). As discussed in Section II-B (2), whether the external motion is removed before or after electronic–nuclear separation has an effect on electronic–nuclear coupling.

we note that

$$H_u = H_0 + T_N \quad (20a)$$

where

$$H_0 = T_E + \mathcal{V} \quad (20b)$$

The further definition of

$$H_1 = \sum_{\alpha=1}^r \left(\frac{m_0}{m_\alpha} \right) \frac{\hbar^2}{2m} \nabla_\alpha^2 \quad (21)$$

so that

$$T_N = \frac{m}{m_0} H_1 \quad (22)$$

yields

$$H_u = H_0 + \kappa^4 H_1 \quad (23)$$

Also, let us symbolize the electronic coordinates as x_j , with $1 \leq j \leq 3n$, and assume a transformation of the nuclear coordinates which divides them into internal (vibrational) coordinates ξ_β , with $1 \leq \beta \leq 3\nu - 6$, and external (rotational and translational) coordinates θ_γ , with $1 \leq \gamma \leq 6$. For diatomic molecules there is the exception $1 \leq \beta \leq 3\nu - 5$ and $1 \leq \gamma \leq 5$, i.e., only one vibrational coordinate and two rotational coordinates exist. It may be observed, then, that $\mathcal{V}$ is not a function of θ_γ when the molecule is not under external force, which is what we will assume:

$$H_0 = H_0(x_j, \xi_\beta) \quad (24a)$$

and

$$H_1 = H_1(\xi_\beta, \theta_\gamma) \quad (24b)$$

Before continuing with the general solution we deal with a somewhat fictitious problem. Its solution will, however, shortly prove to have an important bearing on the more realistic complete solution. If we put $\kappa = 0$ in Eq. (23), this amounts to taking the nuclei to be fixed, as they will have no kinetic energy. One can then attempt the solution of

$$H_0 \varphi_k = E_k \varphi_k \quad (25)$$

where the eigenvalues E_k are electronic energies related to electronic motion in a milieu of fixed nuclei, and φ_k are the corresponding electronic wave functions. In principle, Eq. (25) could be solved for all fixed values of the nuclei (one or more molecules) with $\varphi_k(x_j, \xi_\beta)$ and $E_k(\xi_\beta)$.

However, the procedure we shall employ from here on is not valid for all nuclear configurations, but only for those around an equilibrium configuration. Therefore, supposing $\xi_\beta^{(0)}$ represents such an equilibrium configuration, we try to solve Eq. (25) for the condition that the displacement

$$\xi_\beta - \xi_\beta^{(0)} = \kappa \zeta_\beta \quad (26)$$

which is of the order of a reasonable vibrational displacement, say, κa .

A Taylor's series expansion of the general function $f(\xi_\beta)$ gives

$$f(\xi_\beta) = f(\xi_\beta^{(0)} + \kappa \zeta_\beta) = f^{(0)} + \kappa f^{(1)} + \kappa^2 f^{(2)} + \dots \quad (27)$$

where

$$f^{(0)} = f^{(0)}(\xi_\beta^{(0)}) \quad (28a)$$

$$f^{(1)} = \sum_\beta \xi_\beta \left(\frac{\partial f}{\partial \kappa \zeta_\beta} \right)_{\kappa \zeta_\beta = 0} \quad (28b)$$

$$f^{(2)} = \frac{1}{2!} \sum_{\beta\beta'} \zeta_\beta \zeta_{\beta'} \left(\frac{\partial^2 f}{\partial \kappa \zeta_\beta \partial \kappa \zeta_{\beta'}} \right)_{\kappa \zeta_\beta = 0; \kappa \zeta_{\beta'} = 0} \quad (28c)$$

Applying Eq. (27) with f as H_0 , E_k , and φ_k , substituting the resulting expressions in Eq. (25), and equating coefficients of powers of κ provides the following electronic equations in zeroth, first, and second orders, with the subscript k suppressed:

$$(H_0^{(0)} - E^{(0)})\varphi^{(0)} = 0 \quad (29a)$$

$$(H_0^{(0)} - E^{(0)})\varphi^{(1)} = -(H_0^{(1)} - E^{(1)})\varphi^{(0)} \quad (29b)$$

$$(H_0^{(0)} - E^{(0)})\varphi^{(2)} = -(H_0^{(1)} - E^{(1)})\varphi^{(1)} - (H_0^{(2)} - E^{(2)})\varphi^{(0)} \quad (29c)$$

To return to the general problem, let us substitute Eq. (23) in Eq. (17) to observe

$$(H_0 + \kappa^4 H_1)\psi = W\psi \quad (30)$$

Now, H_1 may be divided into three categories of terms (see, e.g., Reference 20): those which contain $\partial^2/\partial\xi_\beta\partial\xi_{\beta'}$, those which have $\partial/\partial\xi_\beta$ but not $\partial^2/\partial\xi_\beta\partial\xi_{\beta'}$, and those which are not functions of derivatives with respect to ξ_β . These are, respectively, $H_{\xi\xi}$, $H_{\xi\theta}$, and $H_{\theta\theta}$, where it is understood that all may be functions of ξ_β and θ_γ , except $H_{\xi\xi}$, which cannot be a function of θ_γ . Using the fact that

$$\partial/\partial\xi_\beta = (1/\kappa)\partial/\partial\zeta_\beta \quad (31)$$

it is seen that

$$\kappa^4 H_1 = \kappa^2 H_{\zeta\zeta} + \kappa^3 H_{\zeta\theta} + \kappa^4 H_{\theta\theta} \quad (32)$$

where

$$H_{\xi\xi}(\partial^2/\partial\xi_\beta\partial\xi_{\beta'}) = (1/\kappa^2)H_{\zeta\zeta}(\partial^2/\partial\zeta_\beta\partial\zeta_{\beta'}) \quad (32a)$$

and

$$H_{\xi\theta}(\partial/\partial\xi_\beta) = (1/\kappa)H_{\zeta\theta}(\partial/\partial\zeta_\beta) \quad (32b)$$

Expanding $H_{\zeta\zeta}$, $H_{\zeta\theta}$, and $H_{\theta\theta}$ using Eq. (27) we arrive at

$$\kappa^4 H_1 = \kappa^2 H_1^{(2)} + \kappa^3 H_1^{(3)} + \kappa^4 H_1^{(4)} + \dots \quad (33)$$

where

$$H_1^{(2)} = H_{\zeta\zeta}^{(0)} \quad (33a)$$

$$H_1^{(3)} = H_{\zeta\theta}^{(0)} + H_{\zeta\zeta}^{(1)} \quad (33b)$$

$$H_1^{(4)} = H_{\theta\theta}^{(0)} + H_{\zeta\theta}^{(1)} + H_{\zeta\zeta}^{(2)} \quad (33c)$$

Thus we may rewrite the Hamiltonian in the form

$$H = H_0^{(0)} + \kappa H_0^{(1)} + \kappa^2(H_0^{(2)} + H_1^{(2)}) + \dots \quad (34a)$$

Assuming that the wave function ψ has nonzero values over approximately the same ranges for x_j and ξ_β (otherwise it is not physically meaningful to equate coefficients of powers of κ as we do later, mixing the electronic and nuclear equations), one may then expand ψ and W as

$$\psi = \psi^{(0)} + \kappa\psi^{(1)} + \kappa^2\psi^{(2)} + \dots \quad (34b)$$

$$W = W^{(0)} + \kappa W^{(1)} + \kappa^2 W^{(2)} + \dots \quad (34c)$$

where $W^{(1)}$, $W^{(2)}$, $\dots$ are constants. It should be emphasized that the superscripts to ψ and W , and also those to the function χ shortly to be introduced, do not refer to a Taylor's series expansion about $\xi^{(0)}$ as in Eq. (27). The relations (34b) and (34c) are mere formal expansions for the purpose of solution of Eq. (30). Substituting Eq. (34) into Eq. (30) and equating coefficients, we obtain

$$(H_0^{(0)} - W^{(0)})\psi^{(0)} = 0 \quad (35a)$$

$$(H_0^{(0)} - W^{(0)})\psi^{(1)} = -(H_0^{(1)} - W^{(1)})\psi^{(0)} \quad (35b)$$

$$\begin{aligned} (H_0^{(0)} - W^{(0)})\psi^{(2)} = & -(H_0^{(1)} - W^{(1)})\psi^{(1)} \\ & - (H_0^{(2)} + H_1^{(2)} - W^{(2)})\psi^{(0)} \end{aligned} \quad (35c)$$

If we compare Eq. (35a) with Eq. (29a), we notice that

$$E_k^{(0)} = W_k^{(0)} \quad (36)$$

necessarily, and that $\varphi_k^{(0)}(x_j, \xi_\beta^{(0)})$ is a solution of Eq. (35a). However, since we are looking for a general solution $\psi^{(0)}(x_j, \xi_\beta, \theta_\gamma)$, it may be verified that any arbitrary function $\chi^{(0)}(\xi_\beta, \theta_\gamma)$ multiplying $\varphi_k^{(0)}$ is also a solution of Eq. (35a). For the present let us say that with further restrictions to be discovered later, only certain $\chi^{(0)}$, characterized $\chi_0^{(0)}$, will be satisfactory, and so we may write

$$\psi_{k,\sigma}^{(0)} = \varphi_k^{(0)} \chi_{k,\sigma}^{(0)} \quad (37)$$

In Eq. (37) it should be noted that the electronic motion is separable from the nuclear motion except for the parametric dependence of the electronic wave function on the instantaneous values of the nuclear coordinates. It is from the character of this electronic motion that the word "adiabatic" is taken, i.e., the electrons move continuously in the same electronic state independently of the nuclear motion but in accord with the nuclei as if the latter were fixed at their equilibrium positions.*

Let us now try our hand at Eq. (35b). The solution of the homogeneous equation, i.e., setting the right-hand side equal to zero, is again some $\chi(\xi_\beta, \theta_\gamma)$ multiplying $\varphi^{(0)}$, where the subscripts to the wave functions have been suppressed. The solution of the complete equation is determined by the condition that the inhomogeneous part be orthogonal to the solution of the homogeneous equation. Applying this condition to Eqs. (29b) and (35b) and comparing the results leads to the conclusion that

$$E^{(1)} = W^{(1)} \quad (38)$$

Writing

$$W^{(1)} = \sum_{\beta} \zeta_{\beta} \left(\frac{\partial E}{\partial \xi_{\beta}} \right)_{\xi_{\beta} = \xi_{\beta}^{(0)}} \quad (39)$$

and noting that the ζ_{β} are independent, forces the result that the only way $W^{(1)}$ may be a constant is if

$$W^{(1)} = 0 \quad (40a)$$

because

$$\left(\frac{\partial E}{\partial \xi_{\beta}} \right)_{\xi_{\beta} = \xi_{\beta}^{(0)}} = 0 \quad (40b)$$

* This kind of electronic behavior was unfortunately dubbed adiabatic long ago. A better name may be isoelectronic.

This last equation confirms the comment that the $\xi_{\beta}^{(0)}$ must be chosen as an equilibrium configuration. Putting $E^{(1)} = W^{(1)} = 0$ in Eqs. (29b) and (35b) and comparing the results yields $\chi^{(0)}\varphi^{(1)}$ as a particular solution of Eq. (35b). For a general solution of Eq. (35b) we add any solution of the homogeneous equation $\chi^{(1)}\varphi^{(0)}$, where $\chi^{(1)}(\xi_{\beta}, \theta_{\gamma})$ may be determined by later restrictions, so that the general solution $\psi^{(1)}$ may be written:

$$\psi^{(1)} = \chi^{(1)}\varphi^{(0)} + \chi^{(0)}\varphi^{(1)} \quad (41)$$

Substitution of Eqs. (41), (38) and (40a) in Eq. (35c) plus subsequent subtraction of Eq. (29b), multiplied by $\chi^{(1)}$, and Eq. (29c), multiplied by $\chi^{(0)}$, yields

$$\begin{aligned} (H_0^{(0)} - W^{(0)})(\psi^{(2)} - \chi^{(1)}\varphi^{(1)} - \chi^{(0)}\varphi^{(2)}) \\ = -(H_1^{(2)} + E^{(2)} - W^{(2)})\chi^{(0)}\varphi^{(0)} \end{aligned} \quad (42)$$

Applying the orthogonality condition to this inhomogeneous equation leads to the equation which finally determines part of $\chi^{(0)}$:

$$(H_1^{(2)} + E^{(2)} - W^{(2)})\chi^{(0)} = 0 \quad (43)$$

or in more detailed form:

$$\begin{aligned} \left[H_{\xi\xi}^{(0)} \left(\xi_{\beta}^{(0)}, \frac{\partial^2}{\partial \xi_{\beta} \partial \xi_{\beta'}} \right) + \frac{1}{2} \sum_{\beta\beta'} \xi_{\beta} \xi_{\beta'} \left(\frac{\partial^2 E_k}{\partial \xi_{\beta} \partial \xi_{\beta'}} \right)_{\xi_{\beta}, \xi_{\beta'} = \xi_{\beta}^{(0)}, \xi_{\beta'}^{(0)}} \right. \\ \left. - W_{k,\sigma}^{(2)} \right] \chi_{k,\sigma}^{(0)} = 0 \end{aligned} \quad (44)$$

Since the operator on the wave function is independent of θ_{γ} , one has

$$\chi_{k,\sigma}^{(0)}(\xi_{\beta}, \theta_{\gamma}) = \Xi_{k,v}^{(0)}(\xi_{\beta}) P_{r,t}^{(0)}(\theta_{\gamma}) \quad (45a)$$

and

$$W_{k,\sigma}^{(2)} = W_{k,v}^{(2)} \quad (45b)$$

where the subscripts v , r , and t relate to vibration, rotation, and translation, respectively. Again, it is well to emphasize that the superscripts to χ , Ξ , and P , as with those to ψ and W , are introduced formally and are not given by Eq. (27).

If we multiply Eq. (43) by $\mathbf{x}^2$ and express the result in terms of ξ , we have

$$(\mathbf{x}^4 H_{\xi\xi}^{(0)} + \mathbf{x}^2 E_k^{(2)} - \mathbf{x}^2 W_{k,\sigma}^{(2)}) \chi_{k,\sigma}^{(0)}(\xi_{\beta}, \theta_{\gamma}) = 0 \quad (46)$$

Adding $E_k^{(0)}\chi_{k,\sigma}^{(0)} - E_k^{(0)}\chi_{k,\sigma}^{(0)}$, and noting that to the second order in κ

$$\kappa^4 H_{\xi\xi}^{(0)} = T_N \quad (47)$$

and

$$W_{k,v} = E_k^{(0)} + \kappa^2 W_{k,v}^{(2)} \quad (48)$$

we obtain

$$(T_N + E_k(\xi) - W_{k,v})\chi_{k,\sigma}^{(0)}(\xi_\beta, \theta_\gamma) = 0 \quad (49)$$

valid to the second order in κ .

Equation (49) indicates that the electronic energy E_k acts as the potential function for the motion of the nuclei. Indeed, Born and Oppenheimer have shown that such an equation as Eq. (49) is valid to the fourth order in κ , i.e.,

$$(T_N + E_k(\xi) - W_{k,v,r})\chi_{k,v,r}^{(0)}(\xi_\beta, \theta_{\gamma_r}) = 0 \quad (50)$$

where

$$W_{k,v,r} = E_k^{(0)} + \kappa^2 W_{k,v}^{(2)} + \kappa^4 W_{k,v,r}^{(4)} \quad (51)$$

Since the translational motion of the nuclei can always be separated out easily,^{88,18} we have assumed that this has been done in Eq. (50), as indicated by the subscript r on W , χ , and γ . Beyond the fourth order no relatively simple equation such as Eq. (50) exists because of electronic-nuclear interactions. A more general method including such terms is discussed in Section II-B (2).

The program to obtain fairly accurate energies and wave functions, however, is first to solve Eq. (25) for various fixed nuclear positions, and then to solve Eq. (50) using the result of the solution of Eq. (25). If this is done without computational error, the only sizable discrepancy with experiment should be that due to the omission of electronic-nuclear terms, which are more important as the vibrational energy becomes higher. Actually such a program is numerically feasible at present only for diatomic molecules,* and even the results for the hydrogen molecule³⁸ have not as yet been obtained with satisfactory accuracy. In Section III, we discuss the solution of the electronic equation, but we want here to assume that some potential function, $E_k(\xi)$, has been arbitrarily chosen or actually computed. Our further discussion

* See, however, Reference 57 for the utilization of the Born-Oppenheimer approximation in complex molecules by means of the solution of an analogous integral equation.

in this section is consequently restricted to the solution of Eq. (50) for a diatomic molecule.

Assuming a potential function $E_k(R)$ for a diatomic molecule with nuclear masses m_1 and m_2 , the equation for the motion of the nuclei may be written as

$$\left[\frac{-\hbar^2}{2} \left(\frac{\nabla_1^2}{m_1} + \frac{\nabla_2^2}{m_2} \right) + E_k(R) - W \right] \chi_{k,\sigma}^{(0)}(R, \theta_\gamma) = 0 \quad (52)$$

where R is the internuclear distance. If we now eliminate translational motion, the resulting equation for the internal motion of the nuclei will have the form of Eq. (50), i.e.,

$$\left[\frac{-\hbar^2}{2\mu} \nabla^2 + E_k(R) - W_{k,v,r} \right] \chi_{k,v,r}^{(0)}(R, \theta, \phi) = 0 \quad (53)$$

where

$$\mu = \frac{m_1 m_2}{m_1 + m_2} \quad (54)$$

and θ and ϕ are the usual polar coordinates. The preliminary separation of Eq. (53) into R , θ , and ϕ equations is similar to that in the hydrogen atom problem,⁸⁸ and we have immediately

$$\chi_{k,v,r}^{(0)}(R, \theta, \phi) = \Xi_{k,v}(R) \Theta_{KM}(\theta) \Phi_M(\phi) \quad (55)$$

where

$$\Phi_M(\phi) = \frac{1}{\sqrt{2\pi}} e^{iM\phi} \quad (55a)$$

and

$$\Theta_{KM}(\theta) = \left[\frac{(2K+1)(K-|M|)!}{2(K+|M|)!} \right]^{\frac{1}{2}} P_K^{|M|}(\cos \theta) \quad (55b)$$

In Eq. (55) $P_K^{|M|}$ is an associated Legendre function, and K and M are integers with $K \geq 0$ and $-K \leq M \leq K$.

The radial equation, which still contains the electronic energy function $E_k(R)$, takes the form

$$\left\{ \frac{-\hbar^2}{2\mu} \left[\frac{d^2}{dR^2} - \frac{K(K+1)}{R^2} \right] + E_k(R) - W_{k,v,K} \right\} S_{k,v,K}(R) = 0 \quad (56)$$

where

$$S_{k,v,K}(R) = R \Xi_{k,v,K}(R) \quad (57)$$

The solution of Eq. (56) with an arbitrary choice of the potential $E_k(R)$ has been adequately summarized by Pauling and Wilson.⁷⁶ The simplest choice of potential, Hooke's law, is

$$E_k(R) = \frac{1}{2}A(R - R^{(0)})^2 \quad (58)$$

where A is the force constant for the molecule, and $R^{(0)}$ is the equilibrium internuclear distance. When Eq. (58) is substituted into Eq. (56), the wave functions are given as

$$S_{k,v}(\rho) = \left[\left(\frac{\alpha}{\pi} \right)^{\frac{1}{2}} \frac{1}{2^v v!} \right]^{\frac{1}{2}} e^{-(\alpha/2)\rho^2} H_v(\sqrt{\alpha}\rho) \quad (59)$$

where

$$\rho = R - (1 + B)R^{(0)} \quad (60)$$

$$B = \frac{K(K + 1)\sigma}{3K(K + 1)\sigma + \frac{1}{2}A(R^{(0)})^2} \quad (61)$$

$$\alpha = \frac{\mu}{\hbar} \left[\frac{A(R^{(0)})^2 + 6K(K + 1)\sigma}{\mu(R^{(0)})^2} \right]^{1/2} \quad (62)$$

and

$$\sigma = \hbar^2/2\mu(R^{(0)})^2 \quad (63)$$

These relatively simple wave functions, which include Hermite polynomials, H_v , as factors, represent the molecule as vibrating harmonically in accord with the perfect Hooke's-law potential. They are useful for some applications in chemical kinetics, especially when the transitions are between states low in vibrational quantum number. However, for higher quantum numbers this approximation for the wave functions must necessarily be poor, as indeed also are the energies

$$W_{k,v,K} = (v + \frac{1}{2})\hbar^2\alpha/\mu + K(K + 1)\sigma(1 - B) \quad (64)$$

which yield equally spaced vibrational levels.

Although a more accurate treatment is possible with the choice of the Morse⁷⁰ potential

$$E_k(R) = D[1 - e^{-C(R - R^{(0)})}] \quad (65)$$

where C and D are constants to be adjusted by comparison with experiment, the wave functions for this choice are so complex⁷⁷ that their use in further computation is questionable, and resorting

to a wholly numerical or graphical approach may be more appropriate for accurate work. Such an approach has been given by Davidson,²² who shows how the wave functions and energies may be determined for any numerical representation of a potential curve.*

The boundary conditions for the solution of Eq. (56) are

$$S_{k,v,K}(0) = 0 \quad (66)$$

and

$$\int_0^{\infty} |S_{k,v,K}(R)|^2 dR < \infty \quad (67)$$

In order to obtain a numerical solution subject to these boundary conditions, Davidson suggests that

$$V_{k,K}(R) = E_k(R) + \frac{\hbar^2}{2\mu} \frac{K(K+1)}{R^2} \quad (68)$$

be approximated by the step function $Q_{k,K}(R)$ defined by

$$|V_{k,K}(R) - Q_{k,K}(R)| < \varepsilon \quad (0 \leq R \leq \infty) \quad (69a)$$

$$Q_{k,K}(R) = Q_{k,K;j} = \frac{1}{2}[V_{k,K}(R_j) + V_{k,K}(R_{j-1})] \\ (R_{j+1} \leq R \leq R_j) \quad (69b)$$

and

$$R_{j+1} - R_j \leq R_j - R_{j-1} \quad (69c)$$

Then Eq. (56) may be written as

$$\left(\frac{-\hbar^2}{2\mu} \frac{d^2}{dR^2} + Q_{k,K;j} - W_{k,v,K} \right) S_{k,v,K}(R) = 0 \quad (70)$$

for $R_{j+1} \leq R \leq R_j$. By fitting standard solutions⁷² of Eq. (70) with the boundary conditions Davidson has been able to obtain

* In this connection, a semiclassical empirical procedure known as the Rydberg-Klein-Rees (RKR) procedure has been used to determine the potential energy curves from measured vibrational and rotational levels. (See Reference 97 for further references regarding this method and also modifications of the Morse potential.) Although there is no reason to determine energies in relation to an RKR procedure, as these are given, the wave functions may be obtained with the technique suggested by Davidson.

eigenvalues and eigenfunctions for Eq. (56). The method was tested by using a Morse function, and the results then obtained were in substantial agreement with the analytic solutions. It was then applied using the best *a priori* potential function then available for the hydrogen molecule.^{51,38} Unfortunately, a two-point interpolation formula of questionable accuracy was used to obtain the numerical representation of the potential function, and this has masked the cause of the small discrepancy between measured and calculated levels.*

The numerical representations for the wave functions and energies so obtained can then be used in further computation, such as that of transition probabilities. The approach of Davidson is particularly necessary when it is not sufficient to approximate the potential function by a standard Morse function. Such an eventuality arises, for example, if one desires a careful investigation of the size of errors in vibrational and rotational levels induced by the Born–Oppenheimer approximation itself. For such an investigation it is necessary to take an *accurate* numerical representation of an *a priori* potential function and compute the vibrational and rotational energies for comparison with experiment. However, if such a program is to be meaningful, the accuracy of the *a priori* potential function must be of an order greater than the size of the deficiencies due to the Born–Oppenheimer approximation.

(2) Born–Oppenheimer Separation†

Let us presume that the electronic equation, Eq. (25), has been solved. Noting that the functions φ_k form a complete orthonormal set, we may develop the solution of the total time-independent equation, Eq. (17), in full generality and exactness as

$$\psi = \sum_k \Upsilon_k(\xi_\beta, \theta_\gamma) \varphi_k(x_j, \xi_\beta) \quad (71)$$

where the Υ_k remain to be determined. The substitution of Eq. (71) in Eq. (17) with subsequent multiplication by $\varphi_k^\star$ and integration over x_j leads to

* A more elaborate scheme of interpolation is planned (Reference 38).

† See, e.g., Reference 10.

$$(T_N + E_k - W)\Upsilon_k + \sum_{k'} C_{kk'} \Upsilon_{k'} = 0 \quad (72)$$

where

$$C_{kk'} = \sum_{\beta} \frac{1}{m_{\beta}} A_{kk'}^{(\beta)} P_{\beta} + B_{kk'}^{(\beta)} \quad (73)$$

and

$$A_{kk'}^{(\beta)} = \int \varphi_k^{\star} P_{\beta} \varphi_{k'} dx \quad (73a)$$

$$B_{kk'}^{(\beta)} = \frac{1}{2} \int \varphi_k^{\star} P_{\beta}^2 \varphi_{k'} dx \quad (73b)$$

In Eq. (73) the operator P_{β} is $i\hbar\partial/\partial\xi_{\beta}$. For real φ_k it is easily demonstrated that $A_{kk}^{(\beta)} = 0$, so that Eq. (72) may be rearranged as

$$(T_N + E_k + \sum_{\beta} B_{kk}^{(\beta)}/m_{\beta} - W)\Upsilon_k + \sum_{k'} C_{kk'} \Upsilon_{k'} = 0 \quad (74)$$

where the prime on the sum indicates that $k \neq k'$.

In the case of isoelectronic (adiabatic) motion ($C_{kk'} = 0$), Eq. (74) is reduced to

$$(T_N + E_k + \sum_{\beta} B_{kk}^{(\beta)}/m_{\beta} - W)\Upsilon_k = 0 \quad (75)$$

where

$$U_k = E_k + \sum_{\beta} B_{kk}^{(\beta)}/m_{\beta} \quad (76)$$

supplants E_k as the effective potential function for the nuclear motion described by Υ_k . The solution of Eq. (75) will give a complete and accurate account of isoelectronic motion and may be applied to the single stable molecule of Section II-B (1). However, under such circumstances the terms involving $B_{kk}^{(\beta)}$ are usually very small and therefore neglected in ordinary work.*

For nonisoelectronic motion the set of simultaneous equations represented by Eq. (74) must be solved and the results substituted in Eq. (71) to obtain an accurate picture of the general motion. Indeed, Jepsen and Hirschfelder⁴⁶ have computed the small coupling terms in the hydrogen molecule ion. Although the same general procedure is available for larger coupling terms present

* The effect of these terms, which at large distances are sometimes comparable to van der Waals' forces, has been considered in References 102 and 19.

when electronic energy states are closer, special methods based on the "resonance" in such situations have been devised.⁶³

In principle, it is well to separate the external constants of the motion (see Section IV-A) before electronic-nuclear separation, as the remaining motion will then correspond more readily with observables. Jepsen and Hirschfelder find, for example, that electronic-nuclear coupling is decreased if translation is removed prior to the Born-Oppenheimer separation. The same can probably be said for rotational motion, but the difference would be more difficult to compute.

III. INTERACTION OF SPECIES

It is appropriate to introduce separations of motion into Eq. (3) if the solution of the equation is simplified thereby, or if more physically meaningful interpretations thus arise. Therefore, it is certainly reasonable to separate translation and overall rotation; the latter if it is not too complex.¹⁸ Also, as a result of the relative slowness or difficulty in the change of the electronic states of the molecules in "chemical" collision, one may be able to separate the nuclear and electronic motions. However, in a "chemical" collision, changes in vibrational and rotational quantum states of the molecules are likely to occur, and for the purpose of deriving an interaction potential it is therefore not usually desirable to make other separations in the motion, even though one may require further separations to characterize fully the reactant and product molecules.* The standard procedure is to compute the electronic energy of the total microsystem of reacting molecules by means of Eq. (25) for various fixed internuclear distances. The electronic energies of the separated molecules are then subtracted to obtain the interaction energy as a function of the internuclear distances, and this latter function is known as the interaction potential.

This method of solution ignores the effect of electronic-nuclear coupling terms. In Section II-B (2) we discussed the effect of

* For a consideration of interaction potentials for molecules which remain in specific vibrational and rotational states, see Reference 40. This book is also recommended for its discussion of longer-range potentials, which may enter into chemical reactions to a lesser extent.

such terms, which are very important in the event of electronic transitions (nonadiabaticity) or in the case of degenerate electronic states (Jahn-Teller and Renner effects). However, in the simplest reaction within a nondegenerate ground electronic state, as in the *ortho-para* hydrogen conversion, these complicating factors do not arise. Since there is still much to be learned in order to give accurate detailed analyses of such simple reactions, we confine our discussion in this section and in Section IV to adiabatic transitions within nondegenerate electronic states.

For the purposes of chemical kinetics it would be well if we could obtain the interaction potential without recourse to the total microsystem, but, unfortunately, treatments which employ an interaction operator to compute the interaction energy directly are generally not dependable.* An example of such a treatment is the semiempirical method. After critically examining this method in Section III-A, we discuss in Section III-B the status of more exact *a priori* procedures.

Most of the approaches for the approximate computation of electronic energies are based on the assumption that the electrons are independent of one another. We may then write the electronic wave function φ of the system in terms of separable single-electron wave functions φ_i as follows:

$$\varphi = \prod_{i=1}^n \varphi_i \quad (77)$$

As the system under consideration is quite often a single molecule, the φ_i have been called molecular orbitals, and Eq. (77) is then the molecular orbital approximation.

If we have ν nuclei in our system we can write each φ_i as a linear combination of electronic wave functions centered about each nucleus separately:

$$\varphi_i = \sum_{\alpha=1}^{\nu} a_{\alpha i} \varphi_{\alpha}(i) \quad (78)$$

* A recent discussion of this point is given in Reference 61. For some of the earlier work see Reference 43.

where the $\varphi_\alpha(i)$ are known as atomic orbitals and $a_{\alpha i}$ are appropriate coefficients. With the substitution of Eq. (78) in Eq. (77) we derive the general expression

$$\varphi = \prod_{i=1}^n \sum_{\alpha=1}^v a_{\alpha i} \varphi_\alpha(i) \quad (79)$$

For clarity it may be well to write in detail the two-electron, two-nuclei case:

$$\varphi = [a_{\alpha 1} \varphi_\alpha(1) + a_{\beta 1} \varphi_\beta(1)][a_{\alpha 2} \varphi_\alpha(2) + a_{\beta 2} \varphi_\beta(2)] \quad (80)$$

Multiplying out the right-hand side of Eq. (80) leads to terms in $\varphi_\beta(1)\varphi_\alpha(2)$; $\varphi_\alpha(1)\varphi_\beta(2)$; and $\varphi_\alpha(1)\varphi_\alpha(2)$; $\varphi_\beta(1)\varphi_\beta(2)$. The last two terms are ionic, i.e., they refer to that portion of the wave function φ which allows both electrons on the same nucleus. By ignoring these terms we arrive at the valence-bond approximation, so named because it includes only those terms that have a "valence" electron on each nucleus and thus form a valence bond.

Thus, the valence-bond method may be regarded as a special case of the molecular orbital (MO) approximation in a "linear combination of atomic orbitals" (LCAO) modification which omits ionic terms. It should be emphasized, however, that although we have "derived" valence bonds from molecular orbitals, this is not necessary and has been done merely to show the relationship between the two methods. We could just as easily have written *ab initio* the particular linear combination of atomic orbitals which excludes ionic terms.

We may always improve on either of the approximations discussed above by introducing variable parameters and minimizing (e.g., Reference 76)

$$E = \int \varphi^* H \varphi \, dx / \int \varphi^* \varphi \, dx \quad (81)$$

Sometimes it will happen, of course, that although φ is a ground-state wave function for the system under consideration, one must represent the outer (valence) electrons with excited φ_i . If this occurs, care must be taken that in the minimization of Eq. (81) the excited functions are orthogonal to those for the inner shells. Otherwise one will minimize to a fictitious energy representing a state in which all the electrons tend toward their separate ground states.

The application of Eq. (81) in the method of linear variation functions⁷⁶ is important for the later discussion in Sections III-A and III-B. Suppose φ is a sum of linearly independent functions φ_l with arbitrary coefficients multiplying each of these functions, i.e.,

$$\varphi = \sum_l c_l \varphi_l \quad (82)$$

It may then be shown using Eq. (81) that the upper limits for the ground and excited energies are given as the roots of the secular determinant:

$$\begin{vmatrix} H_{11} - \Delta_{11}E & H_{12} - \Delta_{12}E & \cdots & H_{1m} - \Delta_{1m}E \\ H_{21} - \Delta_{21}E & H_{22} - \Delta_{22}E & \cdots & H_{2m} - \Delta_{2m}E \\ \cdots & \cdots & \cdots & \cdots \\ H_{m1} - \Delta_{m1}E & H_{m2} - \Delta_{m2}E & \cdots & H_{mm} - \Delta_{mm}E \end{vmatrix} = 0 \quad (83)$$

where

$$H_{kl} = \int \varphi_k^\star H \varphi_l dx \quad (84a)$$

and

$$\Delta_{kl} = \int \varphi_k^\star \varphi_l dx \quad (84b)$$

A. Critical Exposition of the Semiempirical Method

In developing a modified London formula for later use in the semiempirical method it is traditional²⁷⁻²⁹ to follow a derivation, worked out by Slater,⁹¹ of an approximate expression for the *total* energy, which looks in form exactly like the complementary formula for the *interaction* energy. Then, through a process not made too clear, the modified London formula for the *interaction* energy is applied, even though it has not really been derived. This criticism has been given in detail by Coolidge and James.* A small, but important, change in the Slater procedure gives the proper modified London formula for the interaction energy. It is necessary to belabor the designation of the usual formulas derived as modified because the original as presented by London included other terms which may be regarded as third order.⁵⁹

* See Reference 16, where a derivation of the original London formula is given.

In any event, whether we derive the modified formula for either the total or the interaction energy, we will need Slater's generalization of the valence-bond method. Before we proceed, however, it may be well to warn the reader that the approximations made in deriving and applying the modified London formula are legion and clearly dubious. It is therefore indeed surprising that even rough relative results are obtained.

First, we present a particular basic molecular system which is used for approximate applications in chemical kinetics. The presumption is that many other real systems have some of the character present in this basic system, which we now elaborate. Suppose we have n valence electrons and ν nuclei, where $n = \nu$, and one valence electron is on each nucleus. Valence electrons may be regarded as those which enter more specially into bonding and therefore into a chemical reaction. Further, all the electrons will be in equivalent states. This latter provision means, for example, that all the coefficients of the terms in Eq. (80) are equal except for sign, and that $\varphi_\alpha(i)$ and $\varphi_\beta(i)$ differ from each other only in interchange of equivalent nuclei. It should be noted that if we apply the results derived below to complex systems, i.e., not hydrogen atoms, we have made the doubtful assumption that we may ignore nonvalence electrons.* Moreover, the equivalence of the electronic states implies that we may treat complex systems as if all the valence electrons were in some particular state such as the 1s state.

No quarrel can exist as to the usual separation† of the electronic function $\varphi_\alpha(i)$ into spin functions, α' or β' , and position functions $\varphi'_\alpha(i)$, i.e.,

$$\varphi_\alpha(i) = (\alpha' \text{ or } \beta')\varphi'_\alpha(i) \quad (85)$$

A general valence-bond position function could be

$$\varphi' = \varphi'_\alpha(1)\varphi'_\beta(2) \dots \varphi'_\nu(n) \quad (86)$$

* See Reference 43, where it is shown that this simplification is poor for quantitative work.

† For a discussion of spin and spin functions see, for example, Reference 88.

but any permutation which leaves one electron on each nucleus is still a satisfactory valence-bond position function. Each of these permutations is to be multiplied by appropriate spin functions. An illustration for $n = r = 3$ might be

$$\varphi = \alpha'(1)\beta'(2)\alpha'(3)\varphi'_\alpha(3)\varphi'_\beta(1)\varphi'_\gamma(2) \quad (87)$$

One might suppose that any linear combination of such permuted functions is suitable. Actually, because of the Pauli exclusion principle⁸⁸ only combinations which are antisymmetric with respect to electron interchange are allowed. Slater has shown how to formalize these with the determinant below as the basis:

$$\varphi' = \frac{1}{\sqrt{n!}} \begin{vmatrix} \varphi'_\alpha(1)\varphi'_\beta(1) & \cdots & \varphi'_\gamma(1) \\ \varphi'_\alpha(2)\varphi'_\beta(2) & \cdots & \varphi'_\gamma(2) \\ \vdots & \vdots & \vdots \\ \varphi'_\alpha(n)\varphi'_\beta(n) & \cdots & \varphi'_\gamma(n) \end{vmatrix} \quad (88)$$

Each column of the above determinant is to be multiplied by α' or β' , and since there are 2^n ways of carrying out this multiplication, there are 2^n such determinants representing allowable electronic functions. Any of these may be symbolized as in the following example for $n = 3$,

$$\varphi = \begin{pmatrix} \varphi'_\alpha & \varphi'_\beta & \varphi'_\gamma \\ \alpha' & \alpha' & \beta' \end{pmatrix} \quad (89)$$

where this represents a third-order determinant of the form of Eq. (88), with α' multiplying the first two columns and β' the third column.

As just mentioned, there are 2^n determinants which will satisfy the Pauli exclusion principle. The number may be reduced by considering only those determinants which represent functions that conceivably relate to the formation of a maximum number of bonds. The lowest interaction energy occurs when the number of bonds is at a maximum, and chemical reactions will presumably prefer this lowest energy route. To have a bond the spins must be paired, so it would be helpful to pick only those determinants such that the number of columns with α' is as close as possible to

the number with β' . In this event, for $n = 4$ as an instance, we would reduce $2^n = 16$ determinants to $s = 6$ determinants. This condition may be expressed more elegantly by the statement that we choose only those φ of the original 2^n which satisfy $S_z\varphi = 0$ for an even number of electrons and $S_z\varphi = (\hbar/2)\varphi$ for an odd number of electrons. Here S_z is the z component of the spin angular momentum operator. It turns out, however, as an example given later will clarify, that only s' linear combinations of these s functions may be formed which correspond to maximum bonding, and of these s' , only s'' are linearly independent. Again, the s' are chosen so that $S^2\varphi = 0$ for an even number of electrons, and $S^2\varphi = \frac{3}{4}\hbar^2\varphi$ for an odd number.

For $n = 4$ electrons, we shall now show that $s = 6$, $s' = 3$, and $s'' = 2$. Of the sixteen possible determinants, the $s = 6$ that have spins paired are listed below with Roman numeral subscripts. (The abbreviated notation is used for the determinants with the same positional wave functions in all the total functions.)

	φ'_α	φ'_β	φ'_γ	φ'_δ
φ_I	α'	α'	β'	β'
φ_{II}	α'	β'	α'	β'
φ_{III}	β'	α'	α'	β'
φ_{IV}	α'	β'	β'	α'
φ_V	β'	α'	β'	α'
φ_{VI}	β'	β'	α'	α'

Then, $s' = 3$ linear combinations of these functions may be formed which refer to the maximum number of bonds (two) and still maintain antisymmetry in the electrons. These are

$$\varphi_{\alpha\beta,\gamma\delta} = \frac{1}{\sqrt{4}} (\varphi_{II} - \varphi_{III} - \varphi_{IV} + \varphi_V) \quad (90a)$$

$$\varphi_{\alpha\delta,\beta\gamma} = \frac{1}{\sqrt{4}} (\varphi_I - \varphi_{II} - \varphi_V + \varphi_{VI}) \quad (90b)$$

$$\varphi_{\alpha\gamma,\beta\delta} = \frac{1}{\sqrt{4}} (\varphi_I - \varphi_{III} - \varphi_{IV} + \varphi_{VI}) \quad (90c)$$

where the Greek subscripts are arranged in pairs to represent the bonded nuclei, and the numerical factors are for approximate normalization. Only $s'' = 2$ of these are linearly independent, as

$$\varphi_{\alpha\gamma',\beta\delta} = \varphi_{\alpha\beta,\gamma\delta} + \varphi_{\alpha\delta,\beta\gamma'} \quad (91)$$

We want them linearly independent because we intend to apply Eq. (83).

The question now arises whether we are estimating the total energy or the interaction energy. If we utilize the total Hamiltonian in Eq. (83), we derive a formula for the total energy which is not suitable for direct application in the semiempirical method. On the other hand, if we derive the interaction formula, we require only the interaction terms in the Hamiltonian, but we should be cognizant of the consequences of this method.

As an example, consider the interaction between two molecules, A and B, where the total Hamiltonian for the system is

$$H = H_A + H_B + V \quad (92)$$

Here H_A and H_B are the Hamiltonians of the isolated molecules and V represents the interaction terms. Since E' , the interaction energy, is given by

$$E' = E - E_A - E_B \quad (93)$$

where E is the total energy, and E_A and E_B the energies of the isolated molecules, it is easily shown⁶¹ that

$$E' = \bar{V} + V_0 \quad (94)$$

In Eq. (94) $\bar{V}$ is the result that would be obtained from Eq. (83), with V replacing H and V_0 is written as

$$V_0 = V_{0A} + V_{0B} \quad (95)$$

where

$$V_{0A} = -E_A + \left[\int \varphi^* H_A \varphi dx \right] / \left[\int \varphi^* \varphi dx \right] \quad (96a)$$

and

$$V_{0B} = -E_B + \left[\int \varphi^* H_B \varphi dx \right] / \left[\int \varphi^* \varphi dx \right] \quad (96b)$$

Clearly, V_0 does not vanish unless the actual φ is an eigenfunction of H_A and H_B . In practice, the functions φ are approximated so that they are not usually exact eigenfunctions of the separated

molecules. If A and B are merely hydrogen atoms, then V_0 will vanish, as the functions will indeed be eigenfunctions in Eq. (96). It is important then to realize that in the following procedure we are neglecting V_0 . This omission is sometimes (but only sometimes) balanced by the usual subsequent approximation of neglecting multiple exchange integrals.*

The integrals that arise when determining the actual terms in the determinant of Eq. (83) may be divided into so-called coulomb and exchange integrals. As an illustration to demonstrate the types, let us write one of the integrals that appears when $n = 4$ as

$$I = \int \varphi'_\alpha(1)\alpha'(1)\varphi'_\beta(2)\beta'(2)\varphi'_\gamma(3)\alpha'(3)\varphi'_\delta(4)\beta'(4)(V \text{ or } H) \\ \varphi'_\alpha(1)\alpha'(1)\varphi'_\beta(2)\beta'(2)\varphi'_\gamma(3)\alpha'(3)\varphi'_\delta(4)\beta'(4) dx \quad (97)$$

where complex conjugates are suppressed. The above is a coulomb integral. If, for instance, electrons 2 and 3 with the same spin functions were interchanged with regard to position functions, we would label the resulting exchange integral as $\beta\gamma$. Because of spin orthogonality all nonvanishing integrals must have the same spin functions for the same electrons on both sides of the operator. If we neglect all multiple permutations in integrals such as I , it may easily be shown that this is equivalent to assuming all the functions $\varphi'_\alpha(i)$ in these integrals are orthogonal. This is rather harsh when one considers that interactions depend on overlaps of these functions.

Further details may be gleaned from consulting standard treatises. Suffice it to say here that Eq. (83) with the assumptions discussed above leads, for example, when $n = 4$, to the modified London formula shown below:

$$E^\star = Q - [\tfrac{1}{2}(\alpha\beta + \gamma\delta - \alpha\gamma - \beta\delta)^2 + \tfrac{1}{2}(\alpha\gamma + \beta\delta - \beta\gamma - \alpha\delta)^2 \\ + \tfrac{1}{2}(\beta\gamma + \alpha\delta - \alpha\beta - \alpha\delta)^2]^{\frac{1}{2}} \quad (98)$$

Here $E^\star$ is either E or $\bar{V}$ depending on whether the integrals refer to H or V , and Q is identical with a sum of coulomb integrals between pairs of nuclei:

$$Q = Q_{\alpha\beta} + Q_{\gamma\delta} + Q_{\alpha\gamma} + Q_{\beta\delta} + Q_{\beta\gamma} + Q_{\alpha\delta} \quad (99)$$

* See Reference 62, where the undependable nature of these approximations is demonstrated conclusively. An earlier discussion is given in Reference 16.

To go forward to the semiempirical method²⁶ we must interpret Eq. (98) as a formula for $\bar{V}$, and assume $E' = \bar{V}$. For $n = 2$, the relation analogous to Eq. (98) is

$$E'_{\alpha\beta} = Q_{\alpha\beta} + \alpha\beta \quad (100)$$

The interaction energy $E'_{\alpha\beta}$ represents the binding energy of a diatomic molecule. It is usually known as a function of internuclear distance from an experimentally determined equation, as, for example, a Morse curve. If we have some notion as to the relative proportions of Q_{α} and $\alpha\beta$, we can estimate all the coulomb and exchange integrals for the pairs and substitute into an expression such as Eq. (98) to obtain E' for more complex systems. By judicious variation of the so-called coulomb fraction one can get a fair agreement of E' with experimental determinations thereof. The coulomb fractions ordinarily need not be varied more than from about 1/10 to 3/10, which is close to the theoretical calculation for hydrogen atoms.

In this fashion the method is somewhat successful in deciding between two or more mechanisms for the same reaction. Since about the same coulomb fractions are employed and whatever other errors exist are made in all the computations, relative results are probably satisfactory. However, James and Coolidge⁴⁴ have effectively demonstrated that the coulomb and exchange integrals have no ultimate physical significance. They are merely mathematical forms that arise in a rather approximate treatment of a physical problem. Nevertheless, as a semiempirical tool in the transition-state method largely furthered by Eyring and collaborators, estimates of these integrals have been instrumental in correlating a large amount of data. Still, one cannot push the method too far. If we wish to obtain really accurate and unquestionable results, or if we want special details regarding the reaction mechanism, we should not expect this method to be suitable.*

* An interesting modification of the semiempirical method has been proposed by Sato (Reference 87), and has been extensively discussed by Weston (Reference 100), who concludes that the method "has no more quantum mechanical justification than the original Eyring method".

B. Nonempirical Electronic Energy Computations*

Having decided in Section II-A that the interaction operator technique fails for other than very approximate considerations, we are therefore dependent on the procedure whereby the total electronic energy of the microsystem is determined, and the electronic energies of the parts are subtracted to yield the interaction potential. Even with this approach, however, the inapplicability of simpler methods for the purpose of obtaining accurate interaction potentials is easily illustrated for the system of a hydrogen molecule and hydrogen atom, for which the short-range interaction with all electrons in their ground states has been examined by Aroeste and Jameson.^{5†} Special attention is given to configurations in which the hydrogen atom approaches along a line perpendicular to and bisecting the internuclear axis of the molecule, and is closer than the equilateral triangle position. Clearly, pure valence bonds are undesirable as these give results about 10 to 15 ev higher than the experimental determinations^{3,2‡} in the same range. An improvement 6 to 8 ev higher is made by introducing atomic orbitals for ionic states and varying the coefficients to yield the lowest answers for the total electronic energy, but this is still rather unsatisfactory.||

Aside from possible experimental error, the main discrepancy is apparently due to insufficient provision in the trial wave functions for electronic correlation. A complete account of the background of electronic correlation is given by Löwdin.⁶⁰ Here we

* The author thanks Dr. S. Hagstrom for helpful discussion in relation to this section.

† For longer-range interactions see Reference 62.

‡ The method of interpretation of these experiments has been critized by Wu (Reference 101), with rebuttal by Amdur (Reference 1). Jameson and Aroeste (Reference 45) have suggested that some of the discrepancy may be attributable to the possible presence of electronically excited atoms in the experiment.

|| Another relatively simple approximation is the Hartree-Fock (H-F) self-consistent field (SCF) method, which yields the best *single* Slater determinant for a basis function of the separable type given in Eq. (77). However, this *best* result is generally unsatisfactory for molecular problems, except possibly if it turns out that a correction from more exact computation for one or a few nuclear configurations can be smoothly applied to the approximate result. For a discussion of the H-F (SCF) method see Reference 85.

discuss two of the promising methods which have been applied in the trend toward greater accuracy.

The first of these methods is known as the superposition of (electronic) configurations method. It has been noted^{92,12} that a wave function of any desired accuracy with regard to electron correlation may be obtained by taking a *sum* of a large number of Slater determinants as a trial function in the variation scheme in accord with Eqs. (82), (83), and (84). Each Slater determinant is itself composed of independent one-electron wave functions, and explicit electron interaction is still avoided. Unfortunately, the convergence is slow, and a very large number of determinants may be required for experimental agreement.

Boys and Shavitt¹³ have applied this technique for various fixed nuclear configurations in the interaction of three hydrogen atoms. The basic space orbitals chosen were the following six 1s-type functions:

$$\varphi_1 = N_\alpha e^{-\alpha k r_A} \quad (101a)$$

$$\varphi_2 = N_\beta e^{-\beta k r_A} \quad (101b)$$

$$\varphi_3 = N_\alpha e^{-\alpha k r_B} \quad (101c)$$

$$\varphi_4 = N_\beta e^{-\beta k r_B} \quad (101d)$$

$$\varphi_5 = N_\alpha e^{-\alpha k r_C} \quad (101e)$$

$$\varphi_6 = N_\beta e^{-\beta k r_C} \quad (101f)$$

where

$$N_\alpha = (\alpha^3 k^3 / \pi)^{\frac{1}{2}} \quad (102a)$$

$$N_\beta = (\beta^3 k^3 / \pi)^{\frac{1}{2}} \quad (102b)$$

r_A , r_B , r_C are the distances of the electron from nuclei A, B, C, respectively; α , β are chosen arbitrarily as 1.0, 1.5, respectively; and k is a scale factor which may be varied for optimization. From the functions in Eq. (101) may be obtained 66 linearly independent functions of the type of Eq. (89) or combinations of such functions which satisfy the conditions for the spin angular momentum operator. With these 66 functions Boys and Shavitt proceed to solve Eq. (83) numerically* and obtain thereby the

* Before this may be accomplished, of course, the integrals in Eq. (84) must be evaluated. For tables of such integrals as well as original references and explanatory discussions, see References 52, 66, 79.

best energy values thus far computed for three hydrogen atoms. However, the activation energy, 15.4 kcal/mole, for the reaction $\text{H}_2 + \text{H} \rightarrow \text{H} + \text{H}_2$ determined from their computations is still far from the experimental value, 7 kcal/mole.⁸⁹

Therefore, although it is possible in principle to account for electronic correlation without explicit reference to interelectronic distances, it should be emphasized that for the ground state of the simple system of the isolated hydrogen molecule a virtual check with experiment has been obtained only with explicit inclusion of interelectronic distances.^{44,51} This approach is based on a power series expansion of the wave function, which for the hydrogen molecule may be written as

$$\varphi_{\text{H}_2} = \frac{1}{2\pi} e^{-\delta(\xi_1 + \xi_2)} \sum_{m,n,j,k,p} c_{mnjkp} (\xi_1^m \xi_2^n \eta_1^j \eta_2^k u^p + \xi_1^n \xi_2^m \eta_1^k \eta_2^j u^p) \quad (103)$$

where

$$\xi_1 = (r_{\text{A1}} + r_{\text{B1}})/r_{\text{AB}} \quad (104\text{a})$$

$$\xi_2 = r_{\text{A2}} + r_{\text{B2}}/r_{\text{AB}} \quad (104\text{b})$$

$$\eta_1 = r_{\text{A1}} - r_{\text{B1}}/r_{\text{AB}} \quad (104\text{c})$$

$$\eta_2 = r_{\text{A2}} - r_{\text{B2}}/r_{\text{AB}} \quad (104\text{d})$$

$$u = 2r_{12}/r_{\text{AB}} \quad (104\text{f})$$

r_{12} is the interelectronic distance, r_{AB} is the internuclear distance, δ is a parameter for optimization whose best value is about 0.75, and the variable coefficients c_{mnjkp} are determined by finding the lowest energy in Eq. (83).

Such a method, which is an example of the general category known as the method of correlated wave functions, has not been applied to the system of three hydrogen atoms. Löwdin⁶⁰ has suggested, however, that a powerful tool for the future in computations for more than two electrons may be to multiply the Slater determinants in the superposition of configurations method by a simple correlation factor symmetric with respect to the various interelectronic distances. Although the computation of integrals will be more complex than in the usual superposition of configurations method, the convergence to an accurate result will be more rapid.

IV. COLLISION DYNAMICS

In Section II the object was primarily the description of the states in which separated molecules are found, and in Section III we discussed the interaction between separated molecules. In this section we are concerned with the relationship of the interaction to the relative motion of the molecules, i.e., the transition probability on collision, or the collision cross-section. Naturally, we would want the best interaction potential for any computation of a specific transition probability. However, as we have seen, the potentials are not known as exactly as we would desire; and perhaps this is fortunate because the "correct" potential may complicate the calculation of the transition probability to such an extent that the work would most likely be abandoned, although with machines we may see more rigorous treatments in the future. Indeed, evaluations of collision cross-sections will become more and more important as molecular beam techniques are perfected. The main difficulty in such experiments is detection, but there has been some recent development and application.*

Before examining the relative motion we discuss in Section IV-A the separation of the external motion; then, in Section IV-B we demonstrate for relative motion the equivalence of two first-order approximations, which are unfortunately not of general utility for chemical reactions. In Sections IV-C and IV-D we discuss more exact methods, of which only some have been applied to chemical problems.

A. Separation of External Motion

Considering N particles in Cartesian space-fixed coordinates, we may rewrite Eq. (3) as

$$\left(-\frac{\hbar^2}{2} \sum_{p=1}^N \sum_{s=1}^3 \frac{1}{m_p} \frac{\partial^2}{\partial x_{ps}^2} + V - W \right) \psi = 0 \quad (105)$$

Following Curtiss,¹⁸ we take as an instructive illustration the separation of the external translational motion for the system of two molecules, c and d , with c particles belonging to molecule c ,

* For the application to "chemical" collisions see References 21, 36, 68. For a general discussion see, e.g., Reference 84.

and $N - c$ particles to molecule d. We then change variables from the $3N$ coordinates x_{ps} to the set of coordinates given in the four categories below:

(1) The $3c - 3$ coordinates for molecule c describing its configuration and orientation, choosing coordinates of $c - 1$ particles with respect to the center of mass of molecule c, i.e.,

$$y_{ps} = x_{ps} - \frac{1}{M_c} \sum_{p'=1}^c m_{p'} x_{p's}; \quad (1 \leq p \leq c - 1) \quad (106)$$

where

$$M_c = \sum_{p=1}^c m_p \quad (106a)$$

(2) The $3N - 3c - 3$ coordinates for molecule d, similarly defined:

$$y_{ps} = x_{ps} - \frac{1}{M_d} \sum_{p'=c+1}^N m_{p'} x_{p's}; \quad (c + 1 \leq p \leq N - 1) \quad (107)$$

where

$$M_d = \sum_{p=c+1}^N m_p \quad (107a)$$

(3) The 3 coordinates which state the relative positions of the two centers of mass of the molecules:

$$x_s = \frac{1}{M_c} \sum_{p=1}^c m_p x_{ps} - \frac{1}{M_d} \sum_{p=c+1}^N m_p x_{ps} \quad (108)$$

(4) The 3 coordinates of the center of mass of the total system:

$$X_s = \frac{1}{M} \sum_{p=1}^N m_p x_{ps} \quad (109)$$

where

$$M = M_c + M_d \quad (109a)$$

Substituting Eqs. (106-109) in Eq. (105), we have the result:

$$\left[K_c + K_d - \left(\frac{\hbar^2}{2\mu} \sum_s \frac{\partial^2}{\partial x_s^2} \right) - \left(\frac{\hbar^2}{2M} \sum_s \frac{\partial^2}{\partial x_s^2} \right) + \mathcal{V} - W \right] \psi = 0 \quad (110)$$

where

$$\mu = M_c M_d / M \quad (110a)$$

and

$$K_c = -\frac{\hbar^2}{2} \sum_{p=1}^{c-1} \sum_{p'=1}^{c-1} \sum_s \frac{1}{m_p} \left(\delta_{pp'} - \frac{m_p}{M_c} \right) \frac{\partial^2}{\partial y_{ps} \partial y_{p's}} \quad (111a)$$

$$K_d = -\frac{\hbar^2}{2} \sum_{p=c+1}^{N-1} \sum_{p'=c+1}^{N-1} \sum_s \frac{1}{m_p} \left(\delta_{pp'} - \frac{m_p}{M_d} \right) \frac{\partial^2}{\partial y_{ps} \partial y_{p's}} \quad (111b)$$

With the assumption that $\mathcal{V}$ is independent of X_s (no external force on the system), the following separation of Eq. (110) may be made:

$$\psi = f(X_s) g(x_{ps}, x_s) \quad (112a)$$

$$\left(\frac{-\hbar^2}{2M} \sum_s \frac{\partial^2}{\partial X_s^2} - W_t \right) f = 0 \quad (112b)$$

$$\left(K_c + K_d - \frac{\hbar^2}{2\mu} \sum_s \frac{\partial^2}{\partial x_s^2} + \mathcal{V} - W_i \right) g = 0 \quad (112c)$$

where W_t is the translational energy, and

$$W_i = W - W_t \quad (113)$$

For one molecule, or considering the system as a whole without separating into molecules, Eq. (112c) is reduced to

$$(K_N + \mathcal{V} - W_i) g = 0 \quad (114)$$

where K_N is K_c with N equal to c .

As the overall rotation of a system is likewise unlinked to the potential energy in free space, a separation of this motion may be accomplished.¹⁸ The procedure, however, is rather complicated and is usually not employed, largely because of the degeneracy in the rotational states, which causes the wave function g not to be separable directly as a product, but as a sum of products.

B. First-Order Approximations

(1) First-Order Time-Dependent Perturbation Theory²³

Substitution of Eq. (4) in Eq. (1), also utilizing Eq. (3) with subsequent multiplication of the resulting expression by ψ_j^* , which is any one of ψ_j^* , and integration over all space, leads to

$$i\hbar \dot{a}_j e^{-iW_j t/\hbar} = \sum_j a_j e^{-iW_j t/\hbar} \int \psi_j^* V \psi_j d\tau \quad (115)$$

Defining

$$\omega_{j'j} = (W_{j'} - W_j)/\hbar \quad (116)$$

and

$$V_{j'j} = \int \psi_{j'}^* V \psi_j d\tau \quad (117)$$

Eq. (115) may be transcribed more compactly:

$$\dot{a}_{j'} = (i\hbar)^{-1} \sum_j V_{j'j} a_j e^{i\omega_{j'j}t} \quad (118)$$

Up to and including Eq. (118) it was not really necessary for us to regard V as small, and thus Eq. (118) is exact.

The interaction terms must, however, be small to allow the following perturbation expansion in V , which is most easily accomplished by inserting a categorizing parameter λ such that V is replaced by λV . We expand a_j in a power series, analytic in λ , i.e.,

$$a_j = a_j^{(0)} + \lambda a_j^{(1)} + \lambda^2 a_j^{(2)} + \dots \quad (0 \leq \lambda \leq 1) \quad (119)$$

and place in Eq. (118). By equating coefficients of equal powers of λ and letting the parameter $\lambda = 1$, the following equations result:

$$\dot{a}_{j'}^{(0)} = 0 \quad (120a)$$

$$\dot{a}_{j'}^{(q+1)} = (i\hbar)^{-1} \sum_j V_{j'j} a_j^{(q)} e^{i\omega_{j'j}t} \quad (q = 0, 1, 2, \dots) \quad (120b)$$

The implication of Eq. (120a) is that the $a_{j'}^{(0)}$ are constants. For simplicity we may thus set up the initial unperturbed values of the $a_{j'}^{(0)}$ as we please. Choosing all the $a_{j'}^{(0)} = 0$ save one which we designate $a_{j''}^{(0)} = 1$, we may then integrate the first equation of the set of Eqs. (120b) ($q = 0$) to give

$$a_{j'}^{(1)}(t) = (i\hbar)^{-1} \int_{-\infty}^t V_{j'j''}(t') e^{i\omega_{j'j''}t'} dt' \quad (121)$$

The initial time is taken as $-\infty$, where $a_{j'}^{(1)} = 0$. We have now seemingly lost touch with a_j . However, analysis of the procedure used in obtaining Eq. (115) will indicate that the $a_{j'}$ are really a_j , and we therefore suppress the prime from here on.

With an interaction potential which is constant during a period from $t' = 0$ to $t' = t$ and otherwise zero,* we may reduce Eq. (121) in the new j notation to

$$a_j^{(1)}(t) = \frac{-V_{jj''}}{\hbar} \frac{e^{i\omega_{jj''}t} - 1}{\omega_{jj''}} \quad (122)$$

The probability of finding the system in state j at time t is thus to a first approximation

$$|a_j^{(1)}(t)|^2 = 4|V_{jj''}|^2 \frac{\sin^2 \frac{1}{2}\omega_{jj''}t}{\hbar^2\omega_{jj''}^2} \quad (123)$$

If there is no interference of transition probabilities, i.e., for times sufficiently short so as not to deplete the initial state appreciably, we may define a probability of transition per unit time from the initial state ψ_j as follows:

$$w = t^{-1} \sum_j' |a_j^{(1)}(t)|^2 \quad (124)$$

where the prime signifies that the summation is not necessarily over the complete set, but over subsets hereinafter designated. For example, there may be some range of final states with energy W_j which differs little from $W_{j''}$, and these states may be closely enough dispersed to have a density $\eta(j)$ of states such that $\eta(j)dW_j$ is the number of states in the energy range dW_j . We may then transform Eq. (124) to

$$w = t^{-1} \int |a_j^{(1)}(t)|^2 \eta(j) dW_j \quad (125)$$

With substitution of Eq. (116) and Eq. (123) into Eq. (125), and the further simplification that $V_{jj''}$ and $\eta(j)$ are deemed to be only slowly varying within the subset, one derives

$$w = 4(\hbar t)^{-1} |V_{jj''}|^2 \eta(j) \int_{-\infty}^{+\infty} \frac{\sin^2 \frac{1}{2}\omega_{jj''}t}{\omega_{jj''}^2} d\omega_{jj''} \quad (126)$$

The limits of integration may be extended to $-\infty$ and $+\infty$ because the value of the integral comes primarily from the region $E_j \cong E_{j''}$, presumably, even for the "short" times to which we

* See Reference 4 for a philosophic discussion of such an interaction potential in relation to practical problems in chemical kinetics.

have previously alluded, i.e., $t \gg \hbar/\Delta E$. Evaluation of the definite integral yields

$$w = (2\pi/\hbar)\eta(j)|V_{jj''}|^2 \quad (127)$$

with the result that as a first approximation w is independent of the time.

(2) *Scattering Cross-Section*

Let a beam of particles strike a particle which is at rest in a laboratory system. One may then have coordinates in which the fixed particle is the center. One may also, as we shall do here, choose center-of-mass coordinates for the system composed of the struck and striking particles, where the center of mass of the two particles is at rest at the center of the coordinates. If m_1 is the mass of the struck particle and m_2 is the mass of the striking particle, this is mathematically equivalent to a fictitious particle of reduced mass

$$\mu = m_1 m_2 / (m_1 + m_2) \quad (128)$$

hitting a fixed scattering center placed at the center of mass of the system. The relative speed v of the fictitious particle corresponds to the relative kinetic energy, $\frac{1}{2}\mu v^2$.

Suppose now that we have one scattering center and an incident flux of N particles per unit area per unit time, with the flux small enough for there to be no interference between particles in the beam. Then the number of particles scattered per unit time into a solid angle $d\Omega$ is $N\sigma(\theta, \phi) d\Omega$. Here θ and ϕ are defined with respect to the fixed center of mass, and $\sigma(\theta, \phi)$ is a proportionality factor known as the differential scattering cross-section. The total scattering cross-section is given as

$$\sigma = \int \sigma(\theta, \phi) d\Omega \quad (129)$$

where

$$d\Omega = \sin \theta d\theta d\phi \quad (130)$$

It should be mentioned that the scattering cross-section refers to the asymptotic behavior of the scattered particles, i.e., the behavior after traversing a comparatively large distance from the place of collision. However, one does not usually obtain the asymptotic form without consideration of the general solution.

We shall have instances of this procedure in the ensuing sections. Now, we wish only to find the relationship between the transition probability and the differential scattering cross-section for a particular example.

Assuming our particles are without internal structure and that the functions ψ_j in Eq. (127) are plane waves normalized to unity in a large cubical box, L^3 , the initial state is then given as

$$\psi_{j''}(\mathbf{r}) = L^{-3/2} \exp (ik_{j''} \cdot \mathbf{r}) \quad (131)$$

and any final state is

$$\psi_j(\mathbf{r}) = L^{-3/2} \exp (i\mathbf{k}_j \cdot \mathbf{r}) \quad (132)$$

With an interaction potential $V(\mathbf{r})$ we have

$$V_{jj''} = L^{-3} \int V(\mathbf{r}) \exp (i\mathbf{K} \cdot \mathbf{r}) d\tau \quad (133)$$

where

$$\mathbf{K} = \mathbf{k}_{j''} - \mathbf{k}_j \quad (134)$$

It is understood here that $\mathbf{k}_{j''}$ and $\mathbf{k}_j$ have the same value k and are merely different[†] in direction.

For a particle in a box there are $(L/2\pi)^3 dk_{jx} dk_{jy} dk_{jz}$ states in the wave number range $dk_{jx} dk_{jy} dk_{jz}$, or recalling Eq. (130), we may say that there are $(L/2\pi)^3 k^2 dk \sin \theta d\theta d\phi$ final states scattered into $d\Omega$ within the wave number range. Since

$$E_j = \frac{1}{2}\mu v^2 = \hbar^2 k^2 / 2\mu \quad (135)$$

we see that

$$dE_j = \hbar^2 k dk / 2\mu \quad (136)$$

On substituting for dk in the earlier expression for the number of states in the range dk , we observe that for scattering into $d\Omega$ the density $\eta(j)$ of states in the range dE_j is

$$\eta(j) = \frac{\mu k L^3}{8\pi^3 \hbar^2} d\Omega \quad (137)$$

Taking $\eta(j)$ from Eq. (137) and $V_{jj''}$ from Eq. (133), we note that the transition probability w of Eq. (127) is

$$w = \frac{\mu k}{4\pi^2 \hbar^3 L^3} d\Omega \left| \int V(\mathbf{r}) \exp (i\mathbf{K} \cdot \mathbf{r}) d\tau \right|^2 \quad (138)$$

This is the probability per unit time that an incident particle (fictitious mass μ) in state ψ_j will be found on scattering in state ψ_j within the range dE_j and also in $d\Omega$. Or realizing that the normality condition implies a flux such that there is one incident particle in the box L^3 , then the probability is likewise the fractional number of particles scattered per unit time within dE_j and $d\Omega$. Such an incident flux is

$$N = v/L^3 = \hbar k/\mu L^3 \quad (139)$$

whence we may write

$$w = N\sigma(\theta, \phi) d\Omega = (\hbar k/\mu L^3)\sigma(\theta, \phi) d\Omega \quad (140)$$

For the special case, then, of plane waves normalized to the box L^3 , Eq. (140) gives the relation between the differential scattering cross-section and the transition probability w of Eq. (138), so that we have derived

$$\sigma(\theta, \phi) = (\mu/2\pi\hbar^2)^2 \left| \int V(\mathbf{r}) \exp(i\mathbf{K} \cdot \mathbf{r}) d\tau \right|^2 \quad (141)$$

Note that the derivation of Eq. (141) was based on the Dirac time-dependent perturbation theory. We show in Section IV-B (3) how it may be obtained using another scheme.

(3) Born Approximation⁹

For the moment let us restrict our investigation of the Born approximation to an elastic collision between two particles without internal structure as in Section IV-B (2). Then, K_e and K_d in the time-independent equation, Eq. (112c), are nonexistent, and that equation may be rewritten in the present notation as:

$$[(-\hbar^2/2\mu)\nabla^2 + V(\mathbf{r}) - W_j]\psi_j = 0 \quad (142)$$

Here we know that W_j is given by Eq. (135), and our purpose is to determine the detailed asymptotic behavior of ψ_j so that we may check our previous result for the differential cross-section. An appropriate general form to assume for asymptotic ψ_j , neglecting normalization constants, is

$$\psi_j(r, \theta, \phi) \xrightarrow{r \rightarrow \infty} e^{ikz} + r^{-1}f(\theta, \phi) e^{ikr} \quad (143)$$

The first part of the above wave function is an incident plane wave, and the second part is the scattered wave.

Looking for a form as in Eq. (143), we may start by writing ψ_j as

$$\psi_j(\mathbf{r}) = e^{ikz} + \Lambda_j(\mathbf{r}) \quad (144)$$

Employing Eq. (144) in Eq. (142), we get

$$(\nabla^2 + k^2)\Lambda_j = U(\mathbf{r}) \exp(ikz) + U(\mathbf{r})\Lambda_j \quad (145)$$

where

$$U(\mathbf{r}) = (2\mu/\hbar^2)V(\mathbf{r}) \quad (146)$$

The Born approximation neglects the term $U(\mathbf{r})\Lambda_j$. This is justified if Λ_j is small compared with e^{ikz} , or if $U(\mathbf{r})$ is small compared with k^2 . These conditions are often concurrent and will generally be valid when high-velocity incident particles are involved.

Disregarding the above term, the solution of Eq. (145) can be shown (e.g., reference 71) to be

$$\psi_j(\mathbf{r}) = e^{ikz} - (4\pi)^{-1} \int |\mathbf{r} - \mathbf{r}'|^{-1} e^{ik|\mathbf{r}-\mathbf{r}'|} e^{ikz'} U(\mathbf{r}') d\tau' \quad (147)$$

where the asymptotic expression is

$$\psi_j(\mathbf{r}) \xrightarrow{r \rightarrow \infty} e^{ikz} - (4\pi r)^{-1} e^{ikr} \int U(\mathbf{r}') e^{i\mathbf{K} \cdot \mathbf{r}'} d\tau \quad (148)$$

so that

$$f(\theta, \phi) = (-\mu/2\pi\hbar^2) \int V(\mathbf{r}') e^{i\mathbf{K} \cdot \mathbf{r}'} d\tau' \quad (149)$$

In Eqs. (148) and (149) $\mathbf{K}$ has the same meaning as in Eq. (134), where $\mathbf{k}_{j''}$ is the vector of the initial plane wave along the z axis, and $\mathbf{k}_j$ is the vector in the direction (θ, ϕ) . Since the number of particles scattered into $d\Omega$ per unit time is easily seen to be $N|f(\theta, \phi)|^2 d\Omega$, we may apply the relation

$$\sigma(\theta, \phi) = |f(\theta, \phi)|^2 \quad (150)$$

with Eq. (149), suppressing the primes, to show that Eq. (141) is verified. Thus, taking the asymptotic behavior for the Born approximation solution concurs with assuming plane waves in the approximate first-order time-dependent theory.

(4) *Rearrangement Collisions*

We now proceed to set up equations for a binary rearrangement collision in which molecules a and b meet to form molecules c and d. Again, as in Section IV-B (3) we want to solve Eq. (112c) from either the point of view of the reactants a and b or the products c and d. We choose the latter arbitrarily, as the other approach would be similar. In Eq. (112c) we have separated the terms in the Hamiltonian in keeping with the development in Section IV-A. We now make a different separation* and recast the equations in the notation of the present section:

$$(H - W_j)\psi_j = 0 \quad (151)$$

where

$$H = H_c + H_d + T_{cd} + V_{cd} \quad (152)$$

In Eq. (152), H_c and H_d are the Hamiltonians of the separated molecules; T_{cd} is the relative kinetic energy expressed as

$$T_{cd} = (-\hbar^2/2\mu_{cd})\nabla_{cd}^2 \quad (153)$$

and $V_{cd}(\tau_c, \tau_d, \tau_{cd})$ is the comparatively small interaction potential between molecules c and d. For the separated molecules there exist the following relationships:

$$(H_a - E_{a_l})\psi_{a_l} = 0 \quad (154a)$$

$$(H_b - E_{b_m})\psi_{b_m} = 0 \quad (154b)$$

$$(H_c - E_{c_n})\psi_{c_n} = 0 \quad (154c)$$

$$(H_d - E_{d_p})\psi_{d_p} = 0 \quad (154d)$$

where the first two expressions of Eqs. (154) have been incorporated for later reference.

Continuing with our arbitrary choice to solve Eq. (151) in terms of the complete orthonormal set of final states $\psi_{c_n}\psi_{d_p}$, hereafter abbreviated as ψ_{np} , we may expand

$$\psi_j = \sum_{n,p} F_{np}(\mathbf{r}_{cd})\psi_{np} \quad (155)$$

* All the wave functions should be symmetrized for spin. Here we omit spin, as it may be tacked on at the end of any specific problem (see Reference 88).

where the $F_{np}(\mathbf{r}_{cd})$ are functions depending on the intermolecular vector $\mathbf{r}_{cd}$ between the centers of mass of molecules c and d. Using the Eqs. (151)–(155) yields

$$\sum_{n,p} \psi_{np} (T_{cd} - E_{cn} - E_{dp} - E_j) F_{np} = -V_{cd} \psi_j \quad (156)$$

With manipulation this becomes

$$(\nabla_{cd}^2 + k_{np}^2) F_{np} = \frac{2\mu_{cd}}{\hbar^2} \int \psi_{np}^* V_{cd} \psi_j d\tau_c d\tau_d \quad (157)$$

where

$$k_{np}^2 = (2\mu_{cd}/\hbar^2)(E_j - E_{cn} - E_{dp}) \quad (157a)$$

Equation (157) is an exact expression analogous to the simpler Eq. (145).

As in Section IV-B (3), the Born approximation solution for Eq. (157) entails the replacement of ψ_j with a particular initial-state wave function, which may be written

$$\psi_0 = \psi_{lm} \exp(i\mathbf{k}_{lm} \cdot \mathbf{r}_{ab}) \quad (158)$$

where

$$k_{lm}^2 = (2\mu_{ab}/\hbar^2)(E_j - E_{al} - E_{bm}) \quad (158a)$$

A practical criterion for the validity of this approximation is difficult to develop, but it is usually suitable when the relative velocity is large compared with the internal motions.* One may demonstrate⁷¹ that the asymptotic form of $F_{np}(\mathbf{r}_{cd})$ is

$$F_{np}(\mathbf{r}_{cd}) \xrightarrow{r_{cd} \rightarrow \infty} f_{np}(\theta, \phi) \mathbf{r}_{cd}^{-1} \exp(ik_{np} \mathbf{r}_{cd}) \quad (159)$$

where

$$f_{np}(\theta, \phi) = \frac{-\mu_{cd}}{2\pi\hbar^2} \int \psi_{np}^*(\tau'_c, \tau'_d) \exp(-i\mathbf{k}_{np} \cdot \mathbf{r}_{cd}) V_{cd}(\tau'_c, \tau'_d, \tau'_{cd}) \psi_{lm}(\tau_a^2, \tau_b^2) \exp(i\mathbf{k}_{lm} \cdot \mathbf{r}_{ab}) d\tau'_c d\tau'_d d\tau'_{cd} \quad (160)$$

* In Section IV-C (2) when we are in the midst of a summary of methods pertinent to slow collisions, we specify under what circumstances the Born approximation may be valid for slow collisions. Also, as discussed in Section II, it should be expected that the ψ_{lm} are not necessarily members of the set ψ_{np} , nor orthogonal to ψ_{np} .

All the primed coordinates in the integrand must be transformed before integration with respect to the stated element of integration or its equivalent. The angles (θ, ϕ) relate to $\mathbf{r}_{ed}$ (note the lack of prime), $\mathbf{k}_{np}$ is a vector in the direction of $\mathbf{r}_{ed}$ with magnitude as in Eq. (157a).

For a rearrangement collision the differential scattering cross-section is

$$\sigma_{np}(\theta, \phi) = (v/v_0) |f_{np}(\theta, \phi)|^2 \quad (161)$$

where v and v_0 are respectively the final and initial relative speeds. Since v_0 divided by some standard volume is the flux of incident systems, and since $|f_{np}(\theta, \phi)|^2 v$ divided by the same standard volume is the flux of scattered systems per unit solid angle with the quantum numbers (n, ϕ) , then the cross-section of Eq. (161) is associated with the probability of transition per unit solid angle from a specific incident initial state with quantum numbers (l, m) to any one of the scattered final states (n, ϕ) within a specified wave number or energy range. Again, the same formulas may be gleaned from the time-dependent perturbation theory.

(5) *Application to Chemical Reactions*

A calculation of specific transition probabilities for a chemical reaction has been made by Golden and Peiser.^{30,33} Their computations for the reaction



are based on the first-order time-dependent perturbation theory, and since they use plane waves for translational eigenfunctions, their method is equivalent to the Born approximation. It is one of the few such calculations which is three-dimensional.

As discussed in Section IV-C (2), the conditions for the application of the Born approximation are not always met for the regime of chemical reaction, and the work of Golden and Peiser has been criticized¹⁰⁴ on this basis. Golden³¹ has agreed that his results for the reaction of Eq. (162) may indeed be fortuitous, although the calculations of Bauer and Wu [Section IV-C (1)] perhaps show that the Born approximation is sufficient for this reaction. The main criticism of Yasumori and Sato, however, is founded on computations for the reaction



The results here, which have been independently corroborated by Golden, positively demonstrate the lack of fidelity of the Born approximation.

C. Better Approximate Solutions of the Time-Independent Schrödinger Equation

In this section we will summarize some methods which are more appropriate for slow collisions. Before pursuing these, however, we will deal briefly in Section IV-C (1) with a method of general applicability to spherically symmetric potentials. We do this now because the later elaboration of the slow-collision methods in Sections IV-C (2) to IV-C (4) will show that these are generally feasible only when approximations are made to reduce them at least partially to the methodology of Section IV-C (1). Probably because of their relative complexity, these methods have unfortunately had little or no application to specific chemical reactions.

(1) *Partial Waves*

What we are essentially looking for is the asymptotic behavior of the solution of Eq. (142) with $V(\mathbf{r}) = V(r)$. In this event ψ_j is a function only of θ and r , as the scattering is symmetric about the polar axis z . But we delay consideration of the general spherically symmetric potential while we observe the effect of the simpler potential, $V(r) = 0$, since the solution of the equation

$$(\nabla^2 + k^2)\psi_j = 0 \quad (164)$$

will be needed for comparison when $V(r) \neq 0$.

The eigenfunction for Eq. (164) may be set forth as

$$\psi_j = \exp(ikz) = \exp(ikr \cos \theta) = \sum_{s=0}^{\infty} (2s+1)i^s P_s j_s(r) \quad (165)$$

where P_s are Legendre coefficients and $j_s(r)$ are solutions, bounded at $r = 0$, of

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dj_s}{dr} \right) + \left[k^2 - \frac{s(s+1)}{r^2} \right] j_s = 0 \quad (166)$$

The asymptotic form of $j_s(r)$ is

$$j_s(r) \xrightarrow{r \rightarrow \infty} (kr)^{-1} \sin(kr - \frac{1}{2}s\pi) \quad (167)$$

Similarly, the solution of

$$[\nabla^2 + k^2 - U(r)]\psi_j = 0 \quad (168)$$

may be written*

$$\psi_j = \sum_{s=0}^{\infty} (2s+1) i^s e^{i\lambda_s} P_s J_s(r) \quad (169)$$

where $J_s(r)$ are solutions bounded at $r = 0$ of

$$\frac{1}{r^2} \frac{d}{dr} \left(r^2 \frac{dJ_s}{dr} \right) + \left[k^2 - U(r) - \frac{s(s+1)}{r^2} \right] J_s = 0 \quad (170)$$

and the constants λ_s , which depend on k and $U(r)$, must usually be computed by numerical integration. The asymptotic form of $J_s(r)$ is

$$J_s(r) \xrightarrow{r \rightarrow \infty} (kr)^{-1} \sin(kr - \frac{1}{2}s\pi + \lambda_s) \quad (171)$$

Thus the λ_s are called phase shifts, as they are the difference in phase between the asymptotic behaviors of the solutions of the equations with and without $U(r)$.

Explicitly then, the wave function $\psi_j(r, \theta)$, which represents an incident and scattered wave, is

$$\psi_j = e^{ikr \cos \theta} + f(\theta) r^{-1} e^{ikr} \quad (172)$$

where

$$f(\theta) = (2ik)^{-1} \sum_{s=0}^{\infty} (2s+1) (e^{2i\lambda_s} - 1) P_s(\cos \theta) \quad (173)$$

Each of the terms in Eq. (173) is called a partial wave.

Bauer and Wu⁶ have applied a method involving the phase shifts λ_s . But they find that their results for the reaction of Eq. (162) are approximately the same whether the phase shifts are eliminated from or included in their computation. Setting the λ_s equal to zero is tantamount to a Born approximation. Therefore, the negligible dependence of the results on λ_s supports in a back-handed way the prior work of Golden and Peiser. This support, however, is tenuous because of the differences in the models of the two approaches.

* This solution is valid only if $U(r)$ falls off more rapidly than $1/r$. This excludes coulomb potentials, which would apply, for example, between electrons and bare nuclei, but which are not usual in interactions between molecules in a chemical reaction.

Golden and Peiser use the Eyring–Polanyi potential, whereas Bauer and Wu use an even more simplified potential. Furthermore, Bauer and Wu treat the linear case and do not consider rotation. A major difference is that whereas Golden and Peiser bypass the activated complex and compute transitions between initial and final states, Bauer and Wu have taken the activated complex made up of H_2 and Br as an actual state and have computed probabilities from the initial state to this “activated state”. Then they have merely chosen a “transmission coefficient” of $\frac{1}{2}$ for the transition from the “activated state” to the final state. Undoubtedly, if the interaction potential is well known, the introduction of the “activated state” is an unnecessary complexity, but Bauer and Wu may well be justified in their claim⁷ that the interaction potential is sufficiently mysterious at present to warrant the crutch.

(2) *Distorted Waves*

Here we wish to solve an equation such as Eq. (145) or Eq. (157), but without the Born approximation, which is not ordinarily valid for slow collisions. Equation (145) is for particles without internal structure and Eq. (157) is for rearrangement collisions. It is instructive at this point to introduce the analogous equation for particles with internal structure, but without a rearrangement collision.* Clearly, such an equation may be evolved by regarding the final products in Eq. (157) as a and b instead of c and d. We would then have

$$(\nabla_{ab}^2 + k_{np}^2)F_{np}(\mathbf{r}_{ab}) = (2\mu_{ab}/\hbar^2) \iint \psi_{np}^* V_{ab} \psi_j d\tau_a d\tau_b \quad (174)$$

where the initial states ψ_{lm} , with which we shall soon approximate ψ_j , are now members of the set ψ_{np} and are thus orthogonal to ψ_{np} . On substitution of Eq. (155), transcribed below with $\mathbf{r}_{ab}$ for $\mathbf{r}_{cd}$ and the running indices relabeled with primes,

$$\psi_j = \sum_{n',p'} F_{n'p'}(\mathbf{r}_{ab}) \psi_{n'p'} \quad (175)$$

* For simplicity, this type of collision is that discussed in Sections IV-C (2)–(4). The methods may be generalized to include rearrangement collisions for chemical reactions.

in Eq. (174), we obtain

$$(\nabla_{ab}^2 + k_{np}^2)F_{np}(\mathbf{r}_{ab}) = (2\mu_{ab}/\hbar^2) \sum_{n',p'} V_{n'p',np} F_{n'p'} \quad (176)$$

where

$$V_{n'p',np} = \iint V_{ab} \psi_{n'p'} \psi_{np}^* d\tau_a d\tau_b \quad (177)$$

Having displayed Eqs. (176) and (177) in full subscript language for completeness, before we carry on it would be well to suppress all the "ab" subscripts and abbreviate $n'p'$ and np as n' and n respectively. Equation (176) would then appear as follows:

$$(\nabla^2 + k_n^2)F_n(\mathbf{r}) = \sum_{n'} U_{n'n} F_{n'} \quad (178)$$

In Eq. (178) Born's approximation amounts to taking all the terms in the series as zero with the exception of the one which overlaps with the initial-state function ψ_{lm} , hereafter designated as ψ_l . With the abbreviated notation this term is $U_{ln}F_l$, where, substituting k_l for k_{lm} , F_l has the form

$$F_l = \exp(i\mathbf{k}_l \cdot \mathbf{r}) \quad (179)$$

Despite the fact that the relative velocity is not large with respect to the internal motion, Born's approximation is still fitting if all the matrix elements $U_{n'n}$ are relatively small with U_{ln} the largest of them. This situation does not usually occur for slow collisions, and therefore we are led to make other slightly better approximations in Eq. (178).

We now make the assumption that all nondiagonal matrix elements in Eq. (178) are small, with U_{ln} , perhaps the largest of these, as the only one not disregarded.* We are then led to the set of equations ($n \neq l$):

$$[\nabla^2 + k^2 - U_{ll}]F_l(\mathbf{r}) = 0 \quad (180a)$$

$$[\nabla^2 + k_n^2 - U_{nn}]F_n(\mathbf{r}) = U_{ln}(\mathbf{r})F_l(\mathbf{r}) \quad (180b)$$

Assuming further that U_{ll} is spherically symmetric, Eq. (180b) is reduced to the form of Eq. (168), so that F_l has the asymptotic

* The term with U_{nl} is probably as large, and when we omit it we rationalize that the method followed in the solution of Eqs. (180) is one of successive approximations to the equations derived when U_{nl} is not ignored.

behavior given in Eq. (172). Substitution of such a solution for F_l into Eq. (180b) yields

$$[\nabla^2 + k_n^2 + U_{nn}]F_n(\mathbf{r}) = G_n(r, \theta, \phi) \quad (181)$$

where, as manifested, G_n is a function of r , θ , and ϕ . If U_{nn} is likewise spherically symmetric, the solution, $\mathcal{J}_n(r, \theta)$, of the homogeneous equation again has the form of Eq. (172). Finally, it will then develop⁷¹ that the asymptotic behavior for $F_n(\mathbf{r})$ is

$$F_n(\mathbf{r}) \xrightarrow{r \rightarrow \infty} -\frac{e^{ikr}}{r} \frac{\mu}{2\pi\hbar^2} \int V_{ln}(\mathbf{r}') F_l(r', \theta') \mathcal{J}_n(r', \pi - \Theta) d\tau' \quad (n \neq l) \quad (182)$$

where

$$\cos \Theta = \cos \theta \cos \theta' + \sin \theta \sin \theta' \cos (\phi - \phi') \quad (182a)$$

Note that in Eq. (182) $V_{ln}(\mathbf{r}')$ has not been taken spherically symmetric. Substituting for $V_{ln}(\mathbf{r}')$, we observe that

$$f_n(\theta, \phi) = \frac{-\mu}{2\pi\hbar^2} \int \int \int V(r', \tau'_a, \tau'_b) \psi_l \psi_n^* F_l(r', \theta') \mathcal{J}_n(r', \pi - \Theta) d\tau'_a d\tau'_b d\tau' \quad (183)$$

It is then interesting that Eq. (183) reduces to Eq. (160) with converted notation *and* replacement of F_l and $\mathcal{J}_n$ with plane waves. This latter comment provides us with the name of the method, as the waves F_l and $\mathcal{J}_n$ partially take into account the distortion of the incident and scattered waves caused by the interaction potential, represented in the first instance by $V_{ll}(r)$ and in the second by $V_{nn}(r)$.

(3) Strong Coupling

The need for another form of approximate solution for Eq. (178) appears when $k_l \cong k_n$, where often all $U_{n'n}$ are small enough to overlook except U_{ln} and U_{nl} , which may be rather large. In other words, there is strong coupling between the l and n stages. Equation (178) then reduces to the two coupled equations:

$$(\nabla^2 + k_l^2 - U_{ll})F_l = U_{ln}F_n \quad (184a)$$

$$(\nabla^2 + k_n^2 - U_{nn})F_n = U_{nl}F_l \quad (184b)$$

Equations (184) may be uncoupled in the case of exact resonance when $k_l = k_n = k$. For such collisions it is plausible that $U_{nl} = U_{ln}$ and that $U_{ll} = U_{nn}$, whence Eq. (178) yields with some maneuvering the following set of simultaneous equations:

$$[\nabla^2 + k^2 - (U_{ll} + U_{ln})](F_l + F_n) = 0 \quad (185a)$$

$$[\nabla^2 + k^2 - (U_{ll} - U_{ln})](F_l - F_n) = 0 \quad (185b)$$

With the standard simplification that both U_{ll} and U_{ln} are spherically symmetric, the above equations are reduced to the methodology of Section IV-C (1), and the rest is detail.

For the case of inexact resonance, when we must contend directly with the coupled equations (184), exact analytical solutions are not obtainable. The methods of approximation in this instance have been reviewed by Massey.⁶³

(4) *Perturbed Stationary-State Wave Functions*

We now discuss a possibly more promising approach not dependent on the solution of Eq. (178). We revert to Eq. (151) [with Eqs. (152) and (153)], where we exchange a and b for c and d respectively:

$$[-(\hbar^2/2\mu)\nabla_r^2 + H_a + H_b + V_{ab} - E_j]\psi_j = 0 \quad (186)$$

If we have the solution of

$$[H_a + H_b + V_{ab} - \mathcal{V}_s(r)]\Gamma_s = 0 \quad (187)$$

we may then express ψ_j in terms of the complete orthonormal set Γ_s as follows:

$$\psi_j = \sum_s \Gamma_s(\mathbf{r}, \mathbf{r}_a, \mathbf{r}_b) F_s(\mathbf{r}) \quad (188)$$

where the F_s remain to be determined. The Γ_s are perturbed stationary-state wave functions because they are independent of the relative kinetic energy (stationary) but are perturbed by the potential V_{ab} .

Substitution of Eq. (188) in Eq. (186) with the use of Eq. (187) gives

$$\begin{aligned} \sum_s (\hbar^2/2\mu) [F_s \nabla_r^2 \Gamma_s + 2 \text{grad}_r F_s \text{grad}_r \Gamma_s + \Gamma_s \nabla_r^2 F_s] \\ = \sum_s [\mathcal{V}_s(r) - E_j] \Gamma_s F_s \end{aligned} \quad (189)$$

If Γ_s is real, this lessens the complexity of the equations, and one may obtain⁶⁴

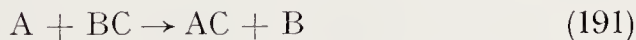
$$[\nabla^2 + (2\mu/\hbar^2)(E_j - \mathcal{V}_s)]F_s = -\sum_{s'} F_{s'} \iint \Gamma_s \nabla_r^2 \Gamma_{s'} d\tau_a d\tau_b \\ - 2 \sum_{s' \neq s} \text{grad}_r F_{s'} \iint \Gamma_s \text{grad}_r \Gamma_{s'} d\tau_a d\tau_b \quad (190)$$

Equation (190) is comparable to Eq. (178). The wave functions, however, are now stipulated by Eqs. (187) and (188), and the interaction potential is supplanted by terms from the small relative kinetic energy. One may treat Eq. (190) as we have Eq. (178), ignoring most of the nondiagonal elements in the series. It is important to understand, nevertheless, that even if such a procedure is adopted, the perturbed stationary-state wave functions still implicitly include some contribution from nondiagonal terms in the sense of Eq. (178). Thus, the method here is of greater accuracy than those based on Eq. (178), but note that Eq. (187) must be solved to apply this method.

D. Numerical Solution of the Time-Dependent Schrödinger Equation

An approach of considerable promise using electronic computers has been put forth by Mazur and Rubin.⁶⁵ They propose a technique wherein the equation is solved numerically for a wave packet representing the initial reactants. The spread of this wave packet into a product region of space determines the reaction probability. Because their primary purpose is to demonstrate the method, Mazur and Rubin make rather vigorous simplifications in their model, which is related to the colinear case of the reaction in Eq. (163).

For a linear system of three atoms undergoing a reaction,



Eq. (1) reduces, after center-of-mass motion is removed, to

$$i\hbar \frac{\partial \Psi}{\partial t} = -\frac{\hbar^2}{2} \left[\left(\frac{1}{m_1} + \frac{1}{m_2} \right) \frac{\partial^2}{\partial r_1^2} + \left(\frac{1}{m_2} + \frac{1}{m_3} \right) \frac{\partial^2}{\partial r_2^2} - \frac{2}{m_2} \frac{\partial^2}{\partial r_1 \partial r_2} \right] \Psi \\ + V(r_1, r_2) \Psi \quad (192)$$

where m_1 , m_2 , and m_3 are the masses of atoms B, C, and A, respectively; r_1 is the distance between B and C; and r_2 is the distance between A and C. Suppose now that we have a wave packet representing the initial state of the system, in which the average relative momentum between A and BC is $P^{(0)}$. Assuming r_2 is rather large at $t = 0$, we can then fairly write the initial wave function Ψ_I at $t = 0$ as

$$\Psi_I = \psi_v(r_1)\psi_{tr}(R, P^{(0)}) \quad (193)$$

where ψ_v is the (internal) vibrational wave function of BC; $R = r_2 + [m_1/(m_1 + m_2)]r_1$ is the distance between A and the center of mass of BC; and the wave function for relative translation, ψ_{tr} , is taken as the one-dimensional Kennard or minimum wave packet (e.g., Reference 88):

$$\psi_{tr} = [2\pi(\Delta R)^2]^{-1/4} \exp [-(R - R^{(0)})^2/4(\Delta R)^2 + iP^{(0)}R/\hbar] \quad (194)$$

In Eq. (194) $(\Delta R)^2$ is the root-mean-square deviation from the mean value $R^{(0)}$.

Mazur and Rubin then follow what happens to the initial wave packet in accord with Eq. (192), which is solved numerically by a finite-difference approximation of a high order of accuracy. By computing the probability of finding part of the packet at a final time t_f in a region such that r_2 is small and r_1 is large, they can thus determine the probability of reaction to a product state.

In principle, the method is applicable with any interaction potential, but the reported calculations neglect the potential, i.e., $V(r_1, r_2) \equiv 0$. Also, although one could take different wave packets representing different velocities, Mazur and Rubin analytically prepare a special wave packet which represents a classical distribution of velocities. With this special wave packet they find that the rate of reaction computed from the Schrödinger equation may differ by a factor of 5 from classical (Hamilton's equation) calculations* with $V(r_1, r_2) \equiv 0$. Since this discrepancy occurs even though the specially prepared wave packet has a superimposed classical character, the results probably would have differed more if this classical compromise were absent. The work

* Similar classical computations with the Eyring-Polanyi potential have been made in Reference 98.

of Mazur and Rubin indicates in any event that a quantum mechanical collision dynamics (aside from a quantum mechanical interaction potential) is necessary for accurate work.

V. MANY-PARTICLE DYNAMICS

In accord with our interest we restrict our exposition in this section to statistical treatments which contain as an element the quantum mechanical cross-section or transition probability discussed in Section IV.* Such statistical approaches which have been applied to chemical reactions may be conveniently divided into three categories: those based on the Pauli equation or similar considerations (Section V-A), a modified Boltzmann equation (Section V-B), or a quantum statistical formulation of the Onsager theory (Section V-C). These treatments have not had notable success in comparison with experiment, probably because of the implicit Born approximation or its equivalent. It is therefore of considerable importance to extend this type of treatment to cross-sections other than that derived with the Born approximation. The method presented in Section V-C would seem to offer the best hope in this direction.

For the sake of clarity we mention here that in the later discussion there are two different processes through which the system seeks equilibrium. We stress, of course, the chemical reaction process leading the system to chemical equilibrium. But at the same time the reactants and products themselves seek equilibrium in their internal and translational states. For simplicity, it is sometimes assumed that the reactants are in an equilibrium distribution during the approach to chemical equilibrium. If the reactants are not in or are allowed to deviate from an initial equilibrium distribution as a result of the ensuing chemical reaction, we then refer to the *nonequilibrium* effect on the chemical reaction rate. All of the methods given in this section are susceptible to the inclusion of such nonequilibrium effects, and we have indicated this in Sections V-A to V-C.

* For recent treatments of a classical bent see References 47, 15, 14, 58. An interesting quantum mechanical discussion has been given in Reference 93 in the language of the scattering matrix, from which the reaction cross-section may be derived.

Here, we first discuss preliminary matters regarding some of the distribution functions used later. Because our exposition in Section V-B is founded on the modification of a classical equation, we include the classical distribution functions as well. For both classical and quantum mechanical considerations, we take a *system* to be a macroscopic object (preferably in gaseous form). A hypothetical collection of such similar systems we call an *ensemble*.

For a classical mechanical system of f degrees of freedom we may define a γ phase space. This is a Euclidian space of $2f$ dimensions, one for each configuration coordinate (configuration space) $q_1 \dots q_f$, and one for each momentum coordinate (momentum space) $p_1 \dots p_f$. The state of each system in the ensemble would be given by a "representative point" in the γ phase space. The state of the ensemble as a whole would then be a "cloud of points" in the γ phase space. We may also define a μ phase space as that of one molecule in the system. If we have N molecules in the system, then the state of the system is determined by one point in γ space or a cloud of N points in μ space. For identical molecules, a cloud of N points in μ space represents the same physical situation with interchange of the N points. And since there are $N!$ different but equivalent arrangements, there are $N!$ points in γ space that correspond to $N!$ equivalent clouds in μ space.

If a large enough number of systems is present in the ensemble, the state of the ensemble may then be specified by a density (distribution function) ρ^γ of representative points in the same γ phase space:

$$\rho^\gamma(p, q, t) = \rho^\gamma(p_1 \dots p_f, q_1 \dots q_f, t) \quad (195)$$

Then, with N' as the number of systems in the ensemble, the mean value $\bar{\mathcal{M}}(p, q, t)$ at time t of some mechanical quantity $\mathcal{M}(p, q)$ (averaged over the ensemble assuming *a priori* probabilities for equal volumes of phase space) is

$$\bar{\mathcal{M}}(p, q, t) = (1/N') \int \dots \int \mathcal{M}(p, q) \rho^\gamma(p, q, t) dp dq \quad (196)$$

since the classical "specific" distribution function

$$\rho_e = \rho^\gamma/N' \quad (197)$$

is the probability, per unit extension in γ phase space, that a system chosen at random would have the values (p, q) at time t .

A few other varieties of distribution function are useful. As mentioned earlier, for N identical molecules there are $N!$ equivalent points in γ space. For such a system we may want a "generic" distribution function

$$f^{(N)} = N! \rho_c \quad (198)$$

which is the probability, averaged over the ensemble, of finding points in any arbitrary order per unit extension in γ space. Also, we can extend the meaning of the several distribution functions to subsets of h molecules chosen from the total of N molecules (see Section V-B).

The time behavior of the classical N -molecule distribution function is contained in Liouville's theorem (e.g., Reference 95):

$$\frac{\partial \rho_c}{\partial t} = - \sum_{j=1}^f \left(\frac{\partial \rho_c}{\partial q_j} \dot{q}_j + \frac{\partial \rho_c}{\partial p_j} \dot{p}_j \right) \quad (199)$$

On substituting Hamilton's equations of motion in Eq. (199) we have

$$\frac{\partial \rho_c}{\partial t} = - \sum_{j=1}^f \left(\frac{\partial \rho_c}{\partial q_j} \frac{\partial H}{\partial p_j} - \frac{\partial \rho_c}{\partial p_j} \frac{\partial H}{\partial q_j} \right) \quad (200)$$

In the notation of Poisson brackets, Eq. (200) may now be rewritten:

$$\frac{\partial \rho_c}{\partial t} = - \{ \rho_c, H \} \quad (201)$$

For a macroscopic quantum mechanical system we may write the wave function for the total system as

$$\Psi = \sum_k c_k(t) \psi_k \quad (202)$$

where ψ_k represents the time-independent portion of the wave function for the system in the state k , and

$$c_k(t) = a_k(t) \exp(-iW_k t/\hbar) \quad (203)$$

We may then define an ensemble density matrix ρ the elements of which are

$$\rho_{nm} = \frac{1}{N!} \sum_{\alpha=1}^{N'} c_{m\alpha}^* c_{n\alpha} = \overline{c_m^* c_n} \quad (204)$$

The diagonal elements ρ_{nn} represent the probability averaged over the ensemble of finding the system in the state n , and the average value of an observable is given by the trace of $\rho \mathcal{M}$, i.e., $\text{tr}(\rho \mathcal{M})$, which we will signify by $\langle \mathcal{M} \rangle_\rho$.

The time-dependent Schrödinger equation, Eq. (1), for such an isolated system yields on substituting Eq. (202)

$$\sum_k c_k H \psi_k = i\hbar \sum_k \dot{c}_k \psi_k \quad (205)$$

On multiplying by ψ_n^* and integrating we obtain

$$\sum_k H_{nk} c_k = i\hbar \dot{c}_n \quad (206)$$

where

$$H_{nk} = \int \psi_n^* H \psi_k d\tau \quad (207)$$

Using Eq. (206), we have

$$i\hbar \frac{\partial \rho_{nm}}{\partial t} = i\hbar (\overline{c_m^* \dot{c}_n} + \overline{\dot{c}_n c_m^*}) = \sum_k (H_{nk} \rho_{km} - \rho_{nk} H_{mk}^*) \quad (208)$$

Since H is Hermitian, we may write Eq. (208) as

$$i\hbar \partial \rho / \partial t = H \rho - \rho H = [H, \rho] \quad (209)$$

which is the quantum mechanical analogue of Liouville's theorem. It is easily seen that a formal solution of Eq. (209) is

$$\rho(t' + \Delta t) = e^{-i\Delta t H / \hbar} \rho(t') e^{i\Delta t H / \hbar} \quad (210)$$

Note that Eqs. (201) and (209) are both reversible in time and refer to isolated systems. They are merely statistical representations of classical mechanics and quantum mechanics, respectively, both of which may be shown to be reversible.⁹⁵ In the methods of the following sections an extra assumption is necessary in order to treat irreversible processes in actual systems, which are not isolated.

A. Pauli Equation

To derive the Pauli equation⁷⁵ we must first extend our discussion of transition probabilities in Section IV. There we treated a transition from a single discrete state to a group of continuous states in an energy range ΔW . Suppose we now have several groups of continuous states within the same energy range ΔW and we want to consider transitions among the groups. We designate the groups of states by Greek letters such as κ , and the states belonging to each of these groups by Latin letters such as k . Furthermore N_κ is the number of k states in the group κ , and $P_\kappa(t)$ is the statistical probability that the system will be found in the group κ at time t . For simplicity we take each of the k states as a single nondegenerate state.* We can then write that

$$P_\kappa = \sum_{k=1}^{N_\kappa} \rho_{kk} = \sum_{k=1}^{N_\kappa} \overline{c_k^\star c_k} = \sum_{k=1}^{N_\kappa} \overline{a_k^\star a_k} \quad (211)$$

The important assumption is now made that for each group at the initial time t_0 we have equal *a priori* probabilities for the existence of each state in a group. Furthermore, the phases of the states are randomly distributed. The latter assumption is equivalent to assuming a diagonal density matrix, and the former asserts that each of the diagonal elements is equal within the group. Therefore, we have

$$\rho_{kk'}(t_0) = \frac{P_\kappa(t_0)}{N_\kappa} \delta_{kk'} \quad (212)$$

It should be realized that Eq. (212) puts the system in such a condition that we are then permitted to observe an irreversible return to equilibrium.

If, in Section IV-B (1), we had not made the assumption that all the $a_{j'} = 0$ save $a_{j''}$, but had carried all the $a_{j'}$, we would have obtained in place of Eq. (122),

$$a_j(t_0 + \Delta t) = a_j(t_0) - \sum_{j'} \frac{V_{jj'}}{\hbar \omega_{jj'}} (e^{i\omega_{jj'} \Delta t} - 1) a_{j'}(t_0) \quad (213)$$

* Degeneracy would merely complicate the notation. Similar equations are obtained involving sums over degeneracies.

where we have changed the initial time to t_0 , and the final time to $t_0 + \Delta t$. With Eqs. (211)–(213) we can then derive similarly to Eq. (213),

$$P_v(t_0 + \Delta t) = P_v(t_0) + \frac{4P_\kappa(t_0)}{N_\kappa} \sum_n \sum_k |V_{nk}|^2 \frac{\sin^2 \omega_{nk} \Delta t}{\hbar^2 \omega_{nk}^2} \quad (214)$$

where we have replaced j by k (belonging to κ) and j' by n (belonging to ν). The sums in Eq. (214) may then become integrations as in Section IV-B (1), and noting that only one integral's limits need be extended to $-\infty$ and $+\infty$, we have

$$\frac{P_v(t_0 + \Delta t) - P_v(t_0)}{\Delta t} = \frac{P_\kappa(t_0)}{N_\kappa} T_{\kappa\nu} \quad (215)$$

where

$$T_{\kappa\nu} = (2\pi\Delta W/\hbar)/V_{nk}|^2 \eta_n \eta_k \quad (216)$$

and η_n , η_k are densities related to the energies, W_n and W_k , respectively.

Considering that there are a number of groups κ from which there may be transitions to a specific group ν , and likewise from the group ν to the various groups, we discern that

$$\frac{P_v(t_0 + \Delta t) - P_v(t_0)}{\Delta t} = \sum_\kappa \left[\frac{T_{\kappa\nu}}{N_\kappa} P_\kappa(t_0) - \frac{T_{\nu\kappa}}{N_\nu} P_\nu(t_0) \right] \quad (217)$$

Since similar equations can be obtained for any time, $t_0 + a\Delta t$, where a is a positive integer, one is tempted to write directly

$$\frac{dP_v(t)}{dt} = \sum_\kappa \left[\frac{T_{\kappa\nu}}{N_\kappa} P_\kappa(t) - \frac{T_{\nu\kappa}}{N_\nu} P_\nu(t) \right] \quad (t \geq t_0) \quad (218)$$

which is the Pauli equation. But this procedure for extending Eq. (217) to longer times is objectionable in that we must make repeated use of the diagonalization assumption.⁴² By noting a certain property of the perturbation, van Hove has derived Eq. (218) with only a single initial diagonalization.⁴¹ It is important to remember, however, that even in van Hove's rigorous derivation of the equation for extended times it is necessary to make the Born approximation or its equivalent.*

* Prigogine and Résibois⁸² have derived the Pauli equation for hard-sphere interactions commonly used in transport processes, but not pertaining to a chemical reaction.

The Pauli equation has, nevertheless, been used to get estimates of reaction rates and also for discussions of nonequilibrium effects.* Montroll and Shuler⁶⁷ have studied a dissociation reaction in a thermal bath of inert molecules. We follow them in utilizing the language of stochastic random-walk processes, although this is not essential.⁷⁴ Each vibrational energy level of a reacting molecule is taken as a point in a one-dimensional walk. There is a reflecting barrier at the lowest level and an absorbing barrier at the highest level (dissociation). When a molecule reaches the highest level, we dispense with it. Thus we can define a mean-first-passage time $\bar{t}$ as the average time it takes molecules to reach and pass the highest level for the first (and only) time. The dissociation rate is thus inversely proportional to $\bar{t}$.

We want to relate $\bar{t}$ to P_v of the Pauli equation. The fraction of undissociated molecules at time t ($0 \leq t \leq \infty$) is $\sum_{v \leq v'} P_v$, where v' is the level next to the highest. The rate at which this fraction is depleted by molecular losses at the highest level is $-\frac{d}{dt} \sum_{v \leq v'} P_v$, and thus we have

$$t = - \int_0^\infty \frac{d}{dt} \sum_{v \leq v'} P_v dt = \int_0^\infty \sum_{v \leq v'} P_v dt \quad (219)$$

If the set of equations represented by Eq. (218) is then written

$$dX(t)/dt = AX(t) \quad (220)$$

where X is a vector of the various P_v , and A is a matrix of the coefficients, it can be shown⁶⁷ that

$$\bar{t} = - \text{tr } A^{-1} \quad (221)$$

After taking the coefficients as the Landau-Teller transition probabilities for the harmonic oscillator,[†] Montroll and Shuler

* Dissociation reactions have been treated in References 67, 90, and 74. The work of Golden and Peiser,^{30,33} discussed with regard to collision dynamics in Section IV-B (5), bears similarities in the statistics to the considerations in developing the Pauli equation. The main difference is that a transition is taken to occur from a discrete state rather than from groups of continuous states.

† In the work of Landau and Teller,⁵⁵ the allowed transition probabilities between nearest levels are all related to the transition probability from the first to the zeroth level.

can then calculate $\bar{t}$. Their work has been extended to a slightly anharmonic oscillator by Kim.⁴⁹ The numerical results from these treatments are not satisfactory when compared with experiment. Montroll and Shuler attribute this to the ignored transitions involving larger quantum jumps. Forgetting about the approximations inherent in the Pauli equation, another possible explanation of the discrepancy with experiment is the failure of the Landau-Teller or similar theories in describing neighboring transitions in the higher levels. Some evidence for this explanation may be extracted from the work of Nikitin and Sokolov,⁷⁴ who pick out the more important higher terms and, albeit with rather crude estimates of these terms, attain fair checks with experiment. It would be well, however, to have more exact computations along these lines before rendering a final judgment.

Aside from the poor comparison with experiment, the work of Montroll and Shuler is interesting in that they give an estimate for the effect on the dissociation rate of a nonequilibrium distribution of vibrational states. This is accomplished by assuming an initial Boltzmann distribution in two computations: one, in which the distribution is artificially maintained throughout the dissociation; and another, in which deviations from equilibrium are allowed. The results show that* when $E_0/kt > 10$, the rates differ by $< 10\%$, and when $E_0/kT = 5$, the difference is about 20% .

B. Modified Boltzmann Equation

Before proceeding we must define one more distribution function analogous to $f^{(N)}$, but for a lesser number of molecules. We can choose h molecules in any order from N identical molecules in $[N!/(N-h)!]$ ways. Therefore,

$$f^{(h)} = [N!/(N-h)!] \rho_c^{(h)} \quad (222)$$

is the probability, averaged over the ensemble, of finding points in any arbitrary order for any subset of h molecules chosen from a total N , where the probability is per unit extension of a γ phase space referred to h molecules. That is, we mean that

$$f^{(h)} = [(N-h)!]^{-1} \int \dots \int f^{(N)} dp^{(N-h)} dq^{(N-h)} \quad (223)$$

* E_0 is the activation energy of the reaction.

As mentioned earlier, the time dependence of distribution functions which are related to the total N molecules is given by the Liouville equation, but no like unique equation valid for $f^{(h)}$ may be extracted from the Liouville expression because of the integrations in Eq. (223). Therefore, some added restriction is required such as the "molecular chaos" assumption described later.

With two-body collisions only (dilute gases),* without chemical reaction for the time being and neglecting finite dimensions of molecules and finite collision times, one may obtain⁴⁰ from the kinetic theory the Boltzmann integro-differential equation for $f^{(1)}$,

$$\begin{aligned} \frac{\partial f_i^{(1)}}{\partial t} + \frac{1}{m_i} \left(\mathbf{p}_i \cdot \frac{\partial f_i^{(1)}}{\partial \mathbf{q}} \right) + \mathbf{X}_i \cdot \frac{\partial f_i^{(1)}}{\partial \mathbf{p}_i} \\ = 2\pi \sum_j \int \int (f_i^{(1)'} f_j^{(1)'} - f_i^{(1)} f_j^{(1)}) g_{ij} b \, db \, d\mathbf{p}_j \end{aligned} \quad (224)$$

In the above, subscripts indicate the species of molecule; the primes are for distribution functions after collision (without primes, before collision), whence the collision integrals with primes are the contributions to $\partial f_i^{(1)}/\partial t$ from collisions (those without primes are for losses from collisions). The impact parameter b is the distance of closest approach between the molecules as if there were no intermolecular force. The relative velocity g_{ij} is

$$g_{ij} = \left| \frac{\mathbf{p}_j}{m_j} - \frac{\mathbf{p}_i}{m_i} \right| \quad (225)$$

and $\mathbf{X}_i$ represents an external force. The primed distribution functions are, of course, implicit functions of the interaction potential, which is spherically symmetric for Eq. (224), as the relationship, $g_{ij} = g'_{ij}$, is necessary for the derivation of this particular form. It should be noted that the summation is over all species, so that when $j = i$ (collision with its own species), the reader should still infer a dummy variable to carry out the integrations. Equation (224) has been derived from the Liouville equation by Kirkwood,^{50†} who examines the effects of finite collision times and finite molecular dimensions, and exhibits the circumstances under which Eq. (224) results. He also explains

* For a dense gas treatment see, e.g., Reference 35.

† For discussions of other derivations see, e.g., Reference 80.

that the derivation depends explicitly on the molecular chaos assumption, i.e., that $f_i^{(1)}$ is independent of $f_j^{(1)}$ if outside a certain distance. This assumption is analogous to the diagonalization assumption required in Section V-A.

Writing the Boltzmann equation in terms of velocity distribution functions, suppressing the superscripts, and assuming uniform conditions and no external forces, yields

$$\frac{\partial f_i}{\partial t} = \sum_j \mathcal{J}(f_i, f_j) \quad (226)$$

where

$$\mathcal{J}(f_i', f_j') = 2\pi \int \int (f_i' f_j' - f_i f_j) g_{ij} b \, db \, d\mathbf{v}_j \quad (227)$$

Enskog's procedure⁴⁰ for solution of an equation such as Eq. (226) involves the introduction of a perturbation parameter λ with an expansion about a condition of local equilibrium, which arises if the LHS of Eq. (226) equals zero. The method entails putting Eq. (226) in the form

$$\frac{\partial f_i}{\partial t} = \frac{1}{\lambda} \sum_j \mathcal{J}(f_i, f_j) \quad (228)$$

with the distribution function as

$$f_i = f_i^{[0]} + f_i^{[1]} + \lambda^2 f_i^{[2]} + \dots \quad (229)$$

The superscripts in $[\]$ are not to be confused with the prior superscripts in $(\)$. When λ is smaller, the frequency of collisions is larger and the mean free path is smaller, whereby there is less deviation from local equilibrium.* Thence, coefficients of equal powers of λ may be equated in the usual fashion to continue with the solution, but it should be mentioned that the convergence of the series in Eq. (229) is open to some doubt.

The Boltzmann theory has been remodeled for polyatomic molecules or molecules with internal states by Wang-Chang and Uhlenbeck.⁹⁹ Their analysis includes distribution functions f_i for each total quantum state i of a molecule (the subscripts now

* For the region of large λ , i.e., large mean free path, see References 48 and 34.

signify different quantum states and not different species), each of which satisfies a Boltzmann-type equation:

$$\frac{\partial f_i}{\partial t} = \sum_{j,k,l} \iint (f'_k f'_l - f_i f_j) g_{ij} \sigma_{kl}(g, \theta, \phi) d\Omega d\mathbf{v}_j \quad (230)$$

Here, i and j stand for initial states, k and l for final states; and $\sigma_{kl}(g, \theta, \phi) d\Omega$, defined for a rearrangement collision in Eq. (161) has been substituted for the classical $2\pi b db$. Equation (230) may be derived from the "quantum mechanical Boltzmann" equation of Uehling and Uhlenbeck⁹⁶ with the assumption of Boltzmann statistics, i.e., that the low-temperature "symmetry" effects of Fermi-Dirac or Bose-Einstein statistics are negligible, but that the quantum mechanical collision cross-section should be retained. We should note that although one may heuristically introduce the quantum mechanical cross-section as in Eq. (230), the Uehling-Uhlenbeck or a similar equation is strictly derived for special interactions only.* In this connection it is interesting that the method given later in Section V-C yields the same result [Eq. (330)] as that of this section [Eq. (251)] only when an approximation equivalent to the Born approximation is made.

The Wang-Chang-Uhlenbeck treatment applies to transitions among internal states without chemical reaction. Eliason and Hirschfelder²⁴ have shown how it can be adapted to chemical reactions, as for example,



In the following we discuss only the forward rate, since the backward rate would be very similar. Associating subscripts a and b with species A and B, subscripts i, j with total quantum states of species A and B, respectively, and subscripts k, l with states of C and D, respectively, we can rewrite Eq. (230) for the forward rate as

$$\frac{\partial f_{ai}}{\partial t} = - \sum_{j,k,l} \mathcal{J}_{j,k,l}^c \quad (232)$$

where

$$\mathcal{J}_{j,k,l}^c = \iint f_{ai} f_{bj} g_{ij} \sigma_{kl}^c d\Omega d\mathbf{v}_{bj} \quad (233)$$

* See, e.g., Reference 69, and also References 42, 82, in which the relationship to the Pauli equation is discussed.

The superscript c emphasizes that we refer to a chemical reaction. We can also define $S_{ij}^{kl}(E)$ as the integral of the differential reaction cross-section $\sigma_{kl}^c(g, \theta, \phi)$:

$$S_{ij}^{kl}(E) = \int \sigma_{kl}^c d\Omega \quad (234)$$

where

$$E = \frac{1}{2} \mu g_{ij}^2 \quad (235)$$

and

$$\mu = m_a m_b / (m_a + m_b) \quad (236)$$

If n_{ai} is the number density for the state i of species A, we observe that

$$n_{ai} = \int f_{ai} d\mathbf{v}_{ai} \quad (237)$$

and assuming we can differentiate under the integral sign, we also have

$$\frac{dn_{ai}}{dt} = \int \frac{\partial f_{ai}}{\partial t} d\mathbf{v}_{ai} \quad (238)$$

With the definition

$$f_{ai}^* = f_{ai} / n_{ai} \quad (239)$$

we obtain from Eqs. (232)–(234), and (238),

$$-\frac{dn_{ai}}{dt} = n_{ai} b_{bj} \sum_{j,k,l} k_{ij}^{kl} \quad (240)$$

where

$$k_{ij}^{kl} = \iint f_{ai}^* f_{bj}^* S_{ij}^{kl}(E) d\mathbf{v}_{ai} d\mathbf{v}_{bj} \quad (241)$$

Then, the total rate of change of species A may be written

$$-\frac{dn_a}{dt} = -\sum_i \frac{dn_{ai}}{dt} = \sum_{i,j,k,l} n_{ai} n_{bj} k_{ij}^{kl} \quad (242)$$

Let us now consider the special case that the reactants are in an equilibrium distribution, both with reference to internal states and also translational states. It is for this special case that we obtain the same result by the method of Section V-C. Before making the assumption for the translational states, however, we stress that Eq. (232) refers to the chemical reaction only, and that we should in principle include terms for collisions without reaction as in Eq. (226). We return to a discussion of this point at the end of this section.

For the present, assuming a Maxwell-Boltzmann velocity distribution⁴⁰ for $f_{ai}^\star$ and $f_{bj}^\star$:

$$f^\star = (m/2\pi kT)^{3/2} \exp(-mv^2/2kT) \quad (243)$$

and changing integration variables in Eq. (241) to

$$\mathbf{G}_{ij} = \frac{m_a}{m_a + m_b} \mathbf{v}_{ai} + \frac{m_b}{m_a + m_b} \mathbf{v}_{bj} \quad (244a)$$

$$\mathbf{g}_{ij} = \mathbf{v}_{ai} - \mathbf{v}_{bj} \quad (244b)$$

one obtains on integrating over $\mathbf{G}_{ij}$ and the angular parts of $\mathbf{g}_{ij}$, and finally using Eq. (235),

$$k_{ij}^{kl} = A(T)Q_{ij}^{kl}(T) \quad (245)$$

where

$$A(T) = (\pi\mu)^{-1/2}(2/kT)^{3/2} \quad (246)$$

and

$$Q_{ij}^{kl}(T) = \int_0^\infty ES_{ij}^{kl}(E) \exp(-E/kT) dE \quad (247)$$

Of possible computational interest is the fact that in Eq. (247) $Q_{ij}^{kl}(T)$ may be regarded as the Laplace transform of $ES_{ij}^{kl}(E)$, and tables of such transforms and their inverses are available.²⁵

If we now further assume an equilibrium distribution in internal states of the reactants, we can write for the partition function, ignoring degeneracies for simplicity,

$$Z_a^{\text{int}} = \sum_i \exp(-\epsilon_{ai}/kT) \quad (248)$$

with the concomitant

$$n_{ai} = \frac{n_a}{Z_a^{\text{int}}} e^{-\epsilon_{ai}/kT} \quad (249)$$

and we thus have from Eq. (242)*

$$-dn_a/dt = k_f n_a n_b \quad (250)$$

where

$$k_f = \frac{A(T)}{Z_a^{\text{int}} Z_b^{\text{int}}} \sum_{i,j,k,l} e^{-(\epsilon_{ai} + \epsilon_{bj})/kT} Q_{ij}^{kl}(T) \quad (251)$$

* Note that we cannot write the usual form of the macroscopic reaction rate expression, Eq. (250), before making the equilibrium assumption in Eq. (249). For a detailed discussion of when Eq. (250) is valid, see Reference 86.

Equations (250) and (251) finally furnish us with a macroscopic rate expression, which may be checked with experimentally determined macroscopic rates. Accurate computations, however, would be rather extensive and none have yet appeared.

We close this section with a brief note on the nonequilibrium effect resulting from the change in the velocity distribution function due to loss of population density in the higher energies because of the reaction. If we consider collisions both with and without reaction we should write a combination of Eqs. (226) and (232):

$$\frac{\partial f_i}{\partial t} = \sum_{j,k,l} (\mathcal{J} - \mathcal{J}^c) \quad (252)$$

Equation (252) can be solved by a modified Enskog or similar procedure. In particular, Present^{78*} has taken a classical $\mathcal{J}^c$ with a reaction cross-section compatible with classical collision theory (e.g., Reference 39). For a reaction of type $A + A \rightarrow B + C$ he finds that for $E_0/kT \geq 5$, the effect causes a difference in rates $< 8\%$. When $E_0/kT < 5$ his first-order approximation becomes progressively worse, and the method is no longer appropriate.

C. Quantum Statistical Formulation of the Onsager Theory

As mentioned earlier the following treatment leads to the same result [Eq. (251)] for the case of an equilibrium distribution of the reactants. Nevertheless, because of the difference in approach and techniques, it is still worthwhile to give in considerable detail an explanation of the method. Also, it can be argued that this method is perhaps less intuitive and hints at a more orderly attack in the future. The discussion here is, however, limited to those chemical reactions which may be regarded as in the class of linear irreversible processes near equilibrium.

We first review in brief those elements of the Onsager theory of irreversible processes (e.g., Reference 37) which are necessary for our development. In general, it may be stated that we observe in nature many irreversible processes which behave such that

* See also References 17, 81, 83, 86, and 94.

fluxes are related by first-order equations to affinities in accord with the phenomenological relation

$$J_i = \sum_{k=1}^n L_{ik} X_k \quad (253)$$

where the J_i are fluxes (for example, a chemical reaction rate), the X_k are affinities (in our case, the chemical affinity), and the L_{ik} are phenomenological coefficients, which for us would be related to reaction rate constants. The flux J_i represents the rate of change of a particular fluctuation α_i , i.e.,

$$J_i = \dot{\alpha}_i \quad (254)$$

and

$$X_k = \frac{\partial \Delta S}{\partial \alpha_k} \quad (255)$$

where ΔS is the deviation of the entropy from its equilibrium value. It is understood that the fluctuations are also measured as deviations from equilibrium values. For a chemical reaction the fluctuations will turn out to be deviations in the numbers of molecules of a species.

Equations (253)–(255) may be given in a form closer to Onsager's assumptions in deriving the reciprocal relations, $L_{ik} = L_{ki}$. We are not especially concerned with these reciprocal relations here, but we are interested in the statement:

$$\frac{\overline{\alpha_i(t' + \Delta t)} - \alpha_i(t')}{\Delta t} = \sum_k L_{ik} \left. \frac{\partial \Delta S}{\partial \alpha_k} \right|_{t=t'} \quad (\Delta t_0 \ll \Delta t \ll \Delta t_r) \quad (256)$$

i.e., it is reasonable to say that the average decay rate of a fluctuation follows the macroscopic phenomenological law if we choose Δt somewhat larger than Δt_0 (some "microscopic" time, as the time between collisions), and also somewhat smaller than Δt_r (the total time for regression to equilibrium for the fluctuation). The bar over $\alpha_i(t' + \Delta t)$ is necessary to average over all the possible values of $\alpha_i(t' + \Delta t)$ which are compatible with the specified values, $\alpha_i(t')$.

If we want to adapt Eq. (256) to quantum statistics* we can write for the same range of Δt

$$\langle \alpha_i \rangle_{\rho(t' + \Delta t)} - \langle \alpha_i \rangle_{\rho(t')} = \Delta t \sum_k L_{ik} \left. \frac{\partial \Delta S}{\partial \alpha'_k} \right|_{t=t'} \quad (257)$$

where α_i is now interpreted as an operator representing a deviation, and

$$\langle \alpha_i \rangle_{\rho(t')} = \alpha'_i \quad (258)$$

In Section V-A it was necessary to invoke diagonalization, and in Section V-B molecular chaos, in order to obtain irreversibility. Here, we are more direct in that Eq. (257) is a statement of irreversibility, *ipso facto*.

To work with Eq. (257) we need a $\rho(t')$ in which we have confidence. On the understanding that we are dealing only with processes near equilibrium, we should choose a $\rho(t')$ similar in form to the density matrix at equilibrium, ρ^e . It is well known that ρ^e has the canonical form⁹⁵

$$\rho^e = \exp [\beta(\Omega^e - H)] \quad (259)$$

where Ω^e is correlated with the thermodynamic free energy and is a scalar quantity, i.e.,

$$\exp (-\beta\Omega^e) = \text{tr} [\exp (-\beta H)] \quad (260)$$

An appropriate form for $\rho(t')$ might then be

$$\rho(t') = \exp \{ \beta [\Omega^e - H + \sum_i A_i(t') \alpha_i] \} \quad (261)$$

where $A_i(t')$ are scalar multipliers, small because of the nearness to equilibrium.

An example in chemical reactions will show that the form given in Eq. (261) is indeed useful. At the same time we demonstrate that this form represents a generalized grand canonical ensemble. The form for the grand canonical ensemble is given by⁹⁵

$$\rho^g = \exp [\beta(\Omega^e - H + \sum_i \mu_i N_i)] \quad (262)$$

* The general procedure described in this section was initiated by Kubo, Yokota, and Nakajima.⁵⁴ The application to chemical reaction rates has been discussed by Yamamoto.¹⁰³

where the μ_i are multipliers known as chemical potentials, and the N_i are operators representing numbers of molecules of species i . Equation (262) is appropriate for the treatment of equilibrium in open systems when the numbers of molecules of the various species, as well as the energy, vary over the ensemble. We now assume that Eq. (262) also holds when there is a slight displacement from equilibrium at time t' . Then, writing

$$N_i = N_i^e + \Delta N_i \quad (263)$$

and taking N_i^e as the null operator in accord with our agreement to measure fluctuations from equilibrium, we have

$$\rho(t') = \exp \{ \beta [\Omega^e - H + \sum_i \mu_i(t') \Delta N_i] \} \quad (264)$$

where $\mu_i(t')$ is identified as $A_i(t')$, and ΔN_i as α_i .

Suppose now that there is a chemical reaction,



where, by convention, a_i are negative integers, and a'_i are positive integers. Defining the chemical affinity as

$$\mathcal{A}(t') = -\sum_i a_i \mu_i(t') - \sum_i a'_i \mu'_i(t') \quad (266)$$

and noting that near chemical equilibrium we can define an operator ΔN such that

$$\langle \Delta N \rangle_\rho = \frac{\langle \Delta N_i \rangle_\rho}{a_i} = \frac{\langle \Delta N'_i \rangle_\rho}{a'_i} \quad (267)$$

we then have from Eq. (264)

$$\rho(t') = \exp \{ \beta [\Omega^e - H - \mathcal{A}(t') \Delta N] \} \quad (268)$$

Equation (268) is used in conjunction with Eq. (257) for the special case where the only deviation from equilibrium is a deviation from chemical equilibrium. In the general case when the states of the reacting species are not in equilibrium, a modification of Eq. (268) to include such deviations is necessary.

Since $\rho(t')$ represents a situation near equilibrium, it is reasonable to make an identification with thermodynamic entropy in the usual way,⁹⁵

$$S = k\langle \log \rho \rangle_\rho \quad (269)$$

whence

$$S = -k\beta(\Omega^e - \langle H \rangle_\rho) + k\beta\mathcal{A}\langle \Delta N \rangle_\rho \quad (270)$$

where

$$\Delta S = k\beta\mathcal{A}\langle \Delta N \rangle_\rho \quad (271)$$

From Eq. (271) we can obtain

$$\left. \frac{\partial \Delta S}{\partial \langle \Delta N \rangle_\rho} \right|_{t=t'} = k\beta\mathcal{A}(t') \quad (272)$$

and rewrite Eq. (257),

$$\langle \Delta N \rangle_{\rho(t'+\Delta t)} - \langle \Delta N \rangle_{\rho(t')} = k\beta L\mathcal{A}(t') \Delta t \quad (273)$$

where L takes the place of L_{ik} .

The form of Eq. (273) indicates we should expand the LHS in a power series in $\mathcal{A}$, which is small near equilibrium. To do this we first set

$$\rho(t') = \exp(\beta\Omega^e)\rho^\star(t') \quad (274)$$

and then expand

$$\rho^\star = B_0 + B_1\mathcal{A} + \dots \quad (275)$$

$$\frac{d\rho^\star}{d\beta} = (-H - \mathcal{A}\Delta N)\rho^\star = B'_0 + \mathcal{A}B'_1 + \dots \quad (276)$$

whence, if we equate coefficients of equal power of $\mathcal{A}$, we find that

$$B_0 = \exp(-\beta H) \quad (277)$$

$$(e^{\beta H} B_1)' = -e^{\beta H} \Delta N e^{-\beta H} \quad (278)$$

Finally, since $B_i = 0$ for $i \geq 1$ when $\beta = 0$, we can integrate Eq. (278) to obtain

$$B_1 = -e^{-\beta H} \int_0^\beta e^{\gamma H} \Delta N e^{-\gamma H} d\gamma \quad (279)$$

with the result that

$$\rho(t') = \rho^e - \mathcal{A}(t') \int_0^\beta \rho^e e^{\gamma H} \Delta N e^{-\gamma H} d\gamma \quad (280)$$

It is convenient to introduce a notation for $e^{\gamma H} \Delta N e^{-\gamma H}$. For this purpose and also for later use we note that consistent with Eq. (210)

$$\langle \Delta N \rangle_{\rho(t' + \Delta t)} = \langle \Delta N(\Delta t) \rangle_{\rho(t')} \quad (281)$$

where

$$\Delta N(\Delta t) = e^{i\Delta t H/\hbar} \Delta N e^{-i\Delta t H/\hbar} \quad (282)$$

Equation (281) is a result of the general rule that matrices may be permuted in cyclic fashion within a trace. As a corollary to Eq. (282) we observe that

$$\Delta N(-i\hbar\gamma) = e^{\gamma H} \Delta N e^{-\gamma H} \quad (283)$$

In this notation we see Eq. (280) as

$$\rho(t') = \rho^e - \mathcal{A}(t') \int_0^\beta \langle \Delta N(-i\hbar\gamma) \rangle_{(\rho^e)} d\gamma \quad (284)$$

Equipped with Eqs. (281) and (284) we now return to Eq. (273) to get

$$\int_0^\beta \langle \Delta N(-i\hbar\gamma) [\Delta N(\Delta t) - \Delta N] \rangle_{(\rho^e)} d\gamma = L' \Delta t \quad (285)$$

where we have set

$$L' = k\beta L \quad (286)$$

Our purpose for the next millenium will be to evaluate L' . To begin we write L' in another form and prove its validity by showing equivalence with Eq. (285). The form is

$$L' = \frac{1}{\Delta t} \int_0^{\Delta t} dt \int_0^t d\tau \int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_{(\rho^e)} d\gamma \quad (287)$$

where $\dot{\Delta N}$ is a time derivative.

In order to proceed with the proof we have to make the reasonable assumption that for the times in the range given for Eq. (256) the rate of approach to equilibrium does not vary with time, i.e., that the rate process is stationary in that range of times. For

such a rate process we may express the condition of temporal homogeneity as

$$\langle \alpha_i(t) \alpha_j(t') \rangle_\rho = \langle \alpha_i(t + \Delta t) \alpha_j(t' + \Delta t) \rangle_\rho \quad (288)$$

Stated in words, average values of correlations between two fluctuations remain constant in time.

Equation (288) is necessary so that we can write the following series of equalities:

$$\begin{aligned} \frac{d^2}{d\tau^2} \int_0^\beta \langle \Delta N(-i\hbar\gamma) \Delta N(\tau) \rangle_\rho d\gamma &= \frac{d}{d\tau} \int_0^\beta \langle \Delta N(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_\rho d\gamma \\ &= \frac{d}{d\tau} \int_0^\beta \langle \Delta N(-\tau - i\hbar\gamma) \dot{\Delta N} \rangle_\rho d\gamma \\ &= - \int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_\rho d\gamma \end{aligned} \quad (289)$$

With Eq. (289) we can transform Eq. (287) to

$$L' = \frac{-1}{\Delta t} \int_0^{\Delta t} dt \int_0^t \left[\frac{d^2}{d\tau^2} \int_0^\beta \langle \Delta N(-i\hbar\gamma) \Delta N(\tau) \rangle_{(\rho^e)} d\gamma \right] d\tau \quad (290)$$

which on performing the integration over τ becomes

$$L' = \frac{-1}{\Delta t} \int_0^{\Delta t} dt \int_{0_1}^\beta [\langle \Delta N(-i\hbar\gamma) \dot{\Delta N}(t) \rangle_{(\rho^e)} - \langle \Delta N(-i\hbar\gamma) \dot{\Delta N} \rangle_{(\rho^e)}] d\gamma \quad (291)$$

Equation (291) may be simplified if we can show that

$$\int_0^\beta \langle \Delta N(-i\hbar\gamma) \dot{\Delta N} \rangle_{(\rho^e)} d\gamma = 0 \quad (292)$$

With the help of Eq. (288) it is easy to see that

$$\int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \Delta N \rangle_{(\rho^e)} d\gamma = \int_0^\beta \langle \Delta N(-i\hbar\gamma) \dot{\Delta N} \rangle_{(\rho^e)} d\gamma \quad (293)$$

The integral on the left may be written as

$$\int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \Delta N \rangle_{(\rho^e)} d\gamma = \frac{1}{i\hbar} [\rho^e, \Delta N] \Delta N = \frac{1}{i\hbar} \rho^e [\Delta N, \Delta N] = 0 \quad (294)$$

The first equality in Eq. (294) follows from the identity⁵³

$$[e^{-\beta H}, \Delta N] = i\hbar \int e^{-\beta H} \dot{\Delta N}(-i\hbar\gamma) d\gamma \quad (295)$$

which may be obtained by noting that consistent with Eq. (282)

$$[H, \Delta N] = -i\hbar \dot{\Delta N} \quad (296)$$

and that

$$\frac{d}{d\beta} \{e^{-\beta H} [\Delta N, e^{-\beta H}]\} = e^{\beta H} [H, \Delta N] e^{-\beta H} \quad (297)$$

Having concluded that Eq. (293) has the badge of validity, we can now integrate the remaining portion of Eq. (291) over t to obtain Eq. (285). This in turn finally proves Eq. (287). With a change in the order of integration in Eq. (287) we then have

$$L' = \int_0^{\Delta t} d\tau (1 - \tau/\Delta t) \int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_{(\rho^e)} d\gamma \quad (298)$$

In order to examine the decay time of the correlation

$$\langle \dot{\Delta N}(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_{(\rho^e)}$$

we realize that it is a correlation of the *rates of change* of fluctuations, and since the fluctuations change only because of collisions, it would be expected that the correlation decays in a time of the order of the collision duration τ' . As Δt is somewhat larger than τ' , we may revise Eq. (298) to give

$$L' \cong \int_0^{\Delta t} d\tau \int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_{(\rho^e)} d\gamma \quad (299)$$

Also, because the decay time of the correlation is so short, we can likewise expect that $\int_{\Delta t}^\infty \ll \int_0^{\Delta t}$, whence

$$L' \cong \int_0^\infty d\tau \int_0^\beta \langle \dot{\Delta N}(-i\hbar\gamma) \dot{\Delta N}(\tau) \rangle_{(\rho^e)} d\gamma \quad (300)$$

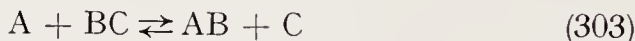
The operators ΔN refer to changes in macroscopic numbers, and if we are to perform computations in terms of microscopic cross-sections, we have to transform Eq. (300) to the microscopic regime. We do this by defining a projection operator (see Section II-A) $\mathcal{P}_i$ to represent all the quantum mechanical states in which the LHS of Eq. (265) exists in the microscopic sense, i.e., a_1 molecules of species A_1 in *any* state, a_2 molecules of species A_2 in *any* state, etc. (Similarly, we can define an operator $\mathcal{P}_r$ for the RHS.) The number operator N_1 may thus be written as

$$N_1 = |a_1| \sum_{l=1}^n \mathcal{P}_l \quad (301)$$

where n is all the possible ways we can get contributions to N_1 , i.e., all the possible combinations of particles for which Eq. (265) could conceivably be satisfied by all the molecules present. Consequently, n is given as

$$n = \binom{\langle N_1 \rangle_\rho}{|a_1|} \binom{\langle N_2 \rangle_\rho}{|a_2|} \cdots + \binom{\langle N'_1 \rangle_\rho}{a'_1} \binom{\langle N'_2 \rangle_\rho}{a'_2} \cdots \quad (302)$$

For a simple example of a specific definition of $\mathcal{P}_i$, let us consider the reaction¹⁰³



Using a configuration criterion (see Section II-A), we can arbitrarily write that

$$\mathcal{P}_i = \sum_k \mathcal{P}_k = I \quad (r_{BC} \leq r_{BC}^0; \ r \geq R) \quad (304a)$$

$$\mathcal{P}_i = 0 \quad (\text{otherwise}) \quad (304b)$$

where r_{BC} is the distance between atoms B and C, r is the distance between A and the center of mass of BC, and k represents a quantum state.

Since

$$\dot{\Delta N} = \dot{N} = - \frac{\dot{N}_1}{|a_1|} = - \sum_{l=1}^n \dot{\mathcal{P}}_l \quad (305)$$

Eq. (300) can now be rewritten as

$$L' = \int_0^\infty d\tau \int_0^\beta d\gamma \left\langle \sum_l^n \sum_{l'}^n \dot{\mathcal{P}}_l (-i\hbar\gamma) \dot{\mathcal{P}}_{l'}(\tau) \right\rangle_{(\rho^e)} \quad (306)$$

If we assume that all the microreactions occur independently, which is the same as neglecting the effect of multiple scattering, then the correlation exists only when $l = l'$, and all cross terms vanish. Therefore, we have

$$L' = \int_0^\infty d\tau \int_0^\beta d\gamma \left\langle \sum_{l=1}^n \dot{\mathcal{P}}_l(-i\hbar\gamma) \dot{\mathcal{P}}_l(\tau) \right\rangle_{(\rho^e)} \quad (307)$$

Finally, we can write Eq. (307) as

$$L' = n \int_0^\infty d\tau \int_0^\beta d\gamma \left\langle \dot{\mathcal{P}}_l(-i\hbar\gamma) \dot{\mathcal{P}}_l(\tau) \right\rangle_{(\rho^e)} \quad (308)$$

when we realize that we have n identical diagonal terms.

The evaluation of the double integral (e.g., Reference 73) in Eq. (308) may now be accomplished. If the eigenfunctions of H are designated as ψ_k with eigenvalues W_k , we have by Eq. (260)

$$\begin{aligned} & \int_0^\beta d\gamma \left\langle \dot{\mathcal{P}}_l(-i\hbar\gamma) \dot{\mathcal{P}}_l(\tau) \right\rangle_{(\rho^e)} \\ &= \left(\sum_k e^{-\beta W_k} \right)^{-1} \sum_k \int_0^\beta (\psi_k | e^{-\beta H} \dot{\mathcal{P}}_l(-i\hbar\gamma) \dot{\mathcal{P}}_l(\tau) | \psi_k) d\gamma \end{aligned} \quad (309)$$

where the notation

$$(\psi_k | A | \psi_k) = A_{kk} \quad (310)$$

is the diagonal matrix element of A in the ψ_k representation. The RHS of Eq. (309) becomes

$$Z^{-1} \sum_k \int_\beta^0 e^{(\gamma-\beta)W_k} (e^{i\tau H/\hbar} \dot{\mathcal{P}}_l \psi_k | e^{-\lambda H} | e^{i\tau H/\hbar} \dot{\mathcal{P}}_l \psi_k) d\gamma \quad (311)$$

with the partition function Z as

$$Z = \sum_k e^{-\beta W_k} \quad (312)$$

and the recognition that $\mathcal{P}_l$ is Hermitian. We then expand

$$e^{i\tau H/\hbar} \dot{\mathcal{P}}_l \psi_k = \sum_{k'} (\psi_{k'} | e^{i\tau H/\hbar} \dot{\mathcal{P}}_l | \psi_k) \psi_{k'} \quad (313)$$

which on substitution in expression (311) and integration over γ , yields from Eq. (308)

$$L' = \frac{n}{Z} \int_0^\infty d\tau \sum_k \sum_{k'} \frac{e^{-\beta W_k} - e^{-\beta W_{k'}}}{W_{k'} - W_k} \operatorname{Re} [(\psi_{k'} | e^{i\tau H/\hbar} \dot{\mathcal{P}}_l | \psi_k) (\psi_k | e^{-i\tau H/\hbar} \dot{\mathcal{P}}_l | \psi_{k'})] \quad (314)$$

where Re , the real part, has been introduced because the imaginary part in the brackets vanishes. The integration over τ finally gives

$$L' = (\beta n \pi \hbar / Z) \sum_k \sum_{k'} e^{-\beta W_k} |(\psi_k | \dot{\mathcal{P}}_l | \psi_{k'})|^2 \delta(W_k - W_{k'}) \quad (315)$$

since

$$\int_0^\infty \cos [\tau(W_k - W_{k'})/\hbar] d\tau = \pi \hbar \delta(W_k - W_{k'}) \quad (316)$$

and

$$\lim_{W_{k'} \rightarrow W_k} \left[\frac{e^{-\beta W_k} - e^{-\beta W_{k'}}}{W_{k'} - W_k} \right] = \beta e^{-\beta W_k} \quad (317)$$

The next step in the continuing effort to find L' in terms of cross-sections is to observe that

$$(\psi_k | \dot{\mathcal{P}}_l | \psi_{k'}) = (i\hbar)^{-1} (W_{k'} - W_k) (\psi_k | \mathcal{P}_l | \psi_{k'}) \quad (318)$$

because of Eq. (296), so that attention then turns to evaluating $(\psi_k | \mathcal{P}_l | \psi_{k'})$. For the reaction in Eq. (303) with the prescription for $\mathcal{P}_l$ of Eq. (304), and using wave functions of the general asymptotic form* for ($r \geq R$; $r_{\text{BC}} \leq r_{\text{BC}}^0$):

$$\psi_k(a) = \varphi(a) e^{i\mathbf{k} \cdot \mathbf{r}} + \sum_{a'} r^{-1} f_{a'} e^{ik'r} \varphi(a') \quad (319a)$$

for states representing the LHS of Eq. (303), and

$$\psi_k(b) = \sum_{a''} r^{-1} f_{a''} e^{ik''r} \varphi(a'') \quad (319b)$$

* See Section IV-B (4). Equation (319) has been written with the expansion of the LHS(a) wave functions. As discussed in Section IV, Eq. (319) can alternatively be written with expansion of the RHS(b) wave functions, and the computations similarly carried through.

for states representing the RHS of Eq. (303). Yamamoto¹⁰³ can then evaluate Eq. (315) as

$$L' = (\beta \hbar n / 8\pi^3 \mu_a Z) \sum_a \sum_b \int d\mathbf{k} e^{-\beta W(k,a)} k S(k,a,b) \quad (320)$$

where $S(k,a,b)$ is in a notation appropriate to this section, being the same as the $S_{ij}^{kl}(E)$ defined in Eq. (234). The inclusion of the summation $\sum_{a'}$ in Eq. (319a) implies that the Born approximation is not being used. However, the simplified form of $\mathcal{P}_l$ causes cancellations in the computation such that the same answer would have been achieved by omitting $\sum_{a'}$ *ab initio*. This indicates an approximation tantamount to a Born approximation.

In order to demonstrate the equivalence with the result of Section V-B [Eq. (251)], we must first relate L' to k_f . Now, for the whole treatment of this section it has been presumed that the reaction is being studied in the linearized form of the phenomenological rate equation. For Eq. (303) the rate equation is expressed as

$$d\langle N_{AB} \rangle_\rho / dt = V^{-1} (k_f \langle N_A \rangle_\rho \langle N_{BC} \rangle_\rho - k_b \langle N_{AB} \rangle_\rho \langle N_C \rangle_\rho) \quad (321)$$

where

$$k_b = k_f \frac{\langle N_A \rangle_{(\rho^e)} \langle N_{BC} \rangle_{(\rho^e)}}{\langle N_{AB} \rangle_{(\rho^e)} \langle N_C \rangle_{(\rho^e)}} \quad (322)$$

Substituting Eq. (322) in Eq. (321), recognizing that

$$\langle N_i \rangle_\rho = \langle N_i \rangle_{(\rho^e)} + \langle \Delta N_i \rangle_\rho \quad (323)$$

and using the linearized expressions valid for ideal gases,³⁷

$$\mu_i = kT \langle \Delta N_i \rangle_\rho / \langle N_i \rangle_{(\rho^e)} \quad (324)$$

we obtain the linearized form of Eq. (321)

$$d\langle N_{AB} \rangle_\rho / dt = (k_f \beta \mathcal{A} / V) \langle N_A \rangle_{(\rho^e)} \langle N_{BC} \rangle_{(\rho^e)} \quad (325)$$

If we dare to write Eq. (273) as

$$d\langle \Delta N \rangle_\rho / dt = d\langle N \rangle_\rho / dt = L' \mathcal{A} \quad (326)$$

and compare it with Eq. (325), we determine that

$$k_f = V L' / \beta \langle N_A \rangle_{(\rho^e)} \langle N_{BC} \rangle_{(\rho^e)} \quad (327)$$

From Eq. (302) we can approximate n as

$$n = \langle N_A \rangle_{(\rho^e)} \langle N_{BC} \rangle_{(\rho^e)} + \langle N_{AB} \rangle_{(\rho^e)} \langle N_C \rangle_{(\rho^e)} \quad (328)$$

which is legitimate as we are omitting terms in $\langle \Delta N_i \rangle_\rho$ higher than first order in the final expression. Writing

$$\frac{\langle N_A \rangle_{(\rho^e)} \langle N_{BC} \rangle_{(\rho^e)}}{n} = \frac{Z_a}{Z} \quad (329)$$

and replacing L' in Eq. (327) with Eq. (321), we have

$$k_f = (\hbar V / 8\pi^3 \mu_a Z_a) \sum_a \sum_b \int d\mathbf{k} e^{-\beta W(k,a)} k S(k,a,b) \quad (330)$$

Finally, one may utilize the following transcriptions:

$$a \rightarrow i,j; \quad b \rightarrow k,l; \quad \mu_a \rightarrow \mu \quad (331)$$

$$S(k,a,b) \rightarrow S_{ij}{}^{kl}(E) \quad (332)$$

$$W(k,a) \rightarrow \varepsilon_{ai} + \varepsilon_{bj} + E \quad (333)$$

$$k^3 dk \rightarrow 2\mu^2 E / \hbar^4 dE \quad (334)$$

$$Z_a \rightarrow Z_a^{\text{int}} Z_b^{\text{int}} V (\mu k T / 2\pi \hbar^2)^{\frac{3}{2}} \quad (335)$$

to show the equivalence of Eq. (330) with Eq. (251).

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ELECTRON GAS IN A LATTICE OF POSITIVE CHARGES

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I. INTRODUCTION

The purpose of the present paper is to study the properties of an electron gas moving in a lattice of positive charges at absolute zero. This picture should correspond roughly to actual metals or metallic solutions and in principle should furnish some new insight into the cohesive properties of pure metals and into the thermodynamic properties of mixing of alloys.

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The cohesive energy of metals has been investigated by various authors. The most important contribution is probably that of Wigner and Seitz^{1,2} who obtained theoretical values of the cohesive energies of alkali metals in rather satisfactory agreement with experiment. One should also mention the calculations of Wigner and Huntington concerning the hypothetical "metallic hydrogen".³ The way in which these problems were treated is as follows: one looked first for approximate Bloch wave functions for independent electrons in the field of ions; then exchange and correlation corrections between the different electrons were taken into account in an approximate way.

The method followed in the present investigation will be entirely different. Its basic idea proceeds from recent work in the field of the quantum electron gas. In 1934 Wigner gave a first approximation to the ground-state energy of an electron gas in a continuous positive background: he calculated exactly the exchange term between a pair of interacting electrons with identical spins and further took into account higher correlations in an approximate way. These correlation terms have been the object of much recent work, especially that of Macke,⁵ Bohm and Pines,⁶⁻⁸ Gell-Mann and Brueckner,⁹ Sawada,¹⁰ and Hubbard.¹¹ In particular, Gell-Mann and Brueckner have shown that at high densities the ground-state energy of an electron gas may be expanded in terms of the interaction strength λ , which is actually proportional to the square of the electronic charge e . The following type of expansion is obtained:

$$E_0 = A + B\lambda + C\lambda^2 \ln \lambda + D\lambda^2 + E\lambda^3 \ln \lambda + \dots \quad (1)$$

where the coefficients $A, B, C, \dots$ are functions of the density; A corresponds to the ideal Fermi gas; B is the exchange term calculated by Wigner;⁴ C has been calculated by Macke⁵ and D by Gell-Mann and Brueckner.⁹ More recently, the coefficient E has been computed by Dubois.^{12,13}

Our idea is to proceed here along the same lines, i.e., to express the properties of an electron gas moving in a lattice of positive charges as an expansion in the interaction strength λ . Thus we shall treat on the same level all electrostatic interactions between pairs of electrons, between pairs of lattice charges and between the electrons and the lattice. Hence we shall make a consistent

expansion of the ground-state energy of such a system in terms of λ up to terms of order λ^2 (i.e., up to the same order as the Gell-Mann and Brueckner expression). This way of proceeding is very different from the Wigner-Seitz method and may eventually be a weaker type of approach on account of the slow convergence of a series such as (1). However, it permits the case of multicomponent lattices (i.e., lattices with more than one type of positive charge located on the sites) to be treated in practically the same way as the one-component lattices. Hence the present method gives some hope for applications to metallic solutions.

Various methods are at our disposal for calculating the ground-state energy of an assembly of interacting fermions. Firstly there are the methods of Brueckner-Goldstone,^{14,15} Hubbard,^{16,11,17} and Hugenholtz¹⁸ which are limited to the ground state. Next, there are more elaborate formalisms which permit the calculation of the thermodynamic properties of a fermion assembly at any desired temperature. In this spirit we may mention the methods of Montroll and Ward,¹⁹ of Bloch and de Dominicis²⁰⁻²² (grand canonical ensemble), and of Brout and Englert²³ (petit canonical ensemble). For convenience we adopt here the method of Bloch and de Dominicis. Let us now briefly indicate the general scheme of our paper.

In Section II we give a detailed account of the perturbation formalism of Bloch and de Dominicis, which for our particular purpose is extended to the case of particles moving in an external potential. Two kinds of expansion of the grand partition function are considered: the first one in powers of the interaction strength λ , the second one in powers of the chemical activity.

In Section III we consider the problem of an electron gas in a lattice of positive point charges from a general point of view. The difficulties related to the long-range character of the electrostatic forces are discussed, and a certain class of divergences are eliminated from the grand partition function through the application of the condition of electroneutrality of the whole system.

In Section IV we treat the case of one-component lattices of point charges, which should constitute a rough model for a metal. Strictly speaking, this model only applies to "metallic hydrogen". A refined model is proposed which takes account in a semi-empirical way of the core structure of actual ions.

In Section V we consider the case of multicomponent lattices of point charges, which should roughly correspond to alloys. We successively treat the cases of a two-component superlattice and of a two-component randomly disordered lattice.

II. GENERAL FORMALISM

Bloch and de Dominicis have derived a general perturbation expansion in powers of the interaction parameter λ for the logarithm of the grand partition function of an N -body system.²⁰ They also re-established the expansion in powers of the activity first derived by Montroll and Ward¹⁹ and showed how one can pass from one formalism to the other.²¹ We shall now sketch the derivation of these results, considering the special case of a system of interacting fermions submitted to an external field.

A. Expansion in Powers of the Interaction Parameter

The grand partition function of a system of mutually interacting identical particles may be written as:

$$\Xi(\alpha, \beta) = \sum_{N=0}^{\infty} e^{\alpha N} \text{Tr } e^{-\beta H_N} \quad (2)$$

where e^{α} is the activity, $\beta = 1/kT$, N is the total number of particles, and H_N is the Hamiltonian operator, the form of which is assumed to be as follows:*

$$H = H_0 + V \quad (3)$$

$$H_0 = -\sum_i \nabla_i^2 \quad (4)$$

$$V = \frac{1}{2} \sum_{i \neq j} v(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_i v'(\mathbf{r}_i) \quad (5)$$

In this expression, v is the two-particle interaction and v' is the interaction between a particle and the external field. All thermodynamic quantities may be deduced from $\Xi(\alpha, \beta)$ through the relation:

$$\begin{aligned} \frac{1}{\beta} \ln \Xi(\alpha, \beta) &= -A(\alpha, \beta) \\ &= \bar{N}\alpha/\beta - F \end{aligned} \quad (6)$$

* We use here a particular system of units such that $\hbar^2/2m = 1$ (m is the mass of a particle).

$A(\alpha, \beta)$ is the Gibbs thermodynamic potential associated with Ξ , F is the usual Helmholtz free energy and $\bar{N}$ is the average number of particles in the system compatible with the value of α :

$$\bar{N} = \frac{\partial}{\partial \alpha} \ln \Xi = -\beta \frac{\partial}{\partial \alpha} A \quad (7)$$

In the second quantization formalism $\Xi(\alpha, \beta)$ may be rewritten as

$$\Xi(\alpha, \beta) = \text{Tr } e^{\alpha N - \beta H} \quad (8)$$

N is now an operator and H is given by

$$H_0 = \sum_r \epsilon_r a_r^+ a_r \quad (9)$$

$$V = \frac{1}{2} \sum_{rstu} \langle rs|v|tu \rangle a_r^+ a_s^+ a_u a_t + \sum_{rs} \langle r|v'|s \rangle a_r^+ a_s \quad (10)$$

$\langle rs|v|tu \rangle$ and $\langle r|v'|s \rangle$ are respectively the matrix elements of v and v' taken between the unperturbed free fermion states ϵ_r , and a_r, a_r^+ are the corresponding destruction and creation operators.

In order to obtain an expansion for $\Xi(\alpha, \beta)$, one uses a formalism similar to the time-dependent perturbation method in quantum mechanics. The grand partition function (8) is rewritten as

$$\Xi(\alpha, \beta) = \text{Tr } e^{\alpha N - \beta H_0} (e^{\beta H_0} e^{-\beta H}) \quad (8')$$

Denoting by $\Xi_0(\alpha, \beta)$ the unperturbed grand partition function and by $\langle O \rangle$ the average value of any operator O taken over the unperturbed system:

$$\langle O \rangle = \text{Tr } e^{\alpha N - \beta H_0} O / \Xi_0(\alpha, \beta) \quad (11)$$

we obtain

$$\Xi(\alpha, \beta) / \Xi_0(\alpha, \beta) = \langle e^{\beta H_0} e^{-\beta H} \rangle \quad (12)$$

Now the operator $e^{\beta H_0} e^{-\beta H}$ obeys the following differential equation:

$$\frac{\partial}{\partial \beta} (e^{\beta H_0} e^{-\beta H}) = -V(\beta) (e^{\beta H_0} e^{-\beta H})$$

the solution of which is

$$e^{\beta H_0} e^{-\beta H} = \sum_{n=0}^{\infty} (-)^n \int_0^{\beta} dt_1 \int_0^{t_1} dt_2 \dots \int_0^{t_{n-1}} dt_n V(t_1) V(t_2) \dots V(t_n) \quad (13)$$

The "time-dependent" operator $V(t)$ is here defined as

$$V(t) = e^{tH_0} V e^{-tH_0}$$

and its explicit form is as follows [cf. Eq. (10)]:

$$V(t) = \frac{1}{2} \sum_{rstu} \langle rs|v|tu \rangle a_r^+ a_s^+ a_u a_t e^{t(\epsilon_r + \epsilon_s - \epsilon_u - \epsilon_t)} + \sum_{rs} \langle r|v'|s \rangle a_r^+ a_s e^{t(\epsilon_r - \epsilon_s)} \quad (14)$$

Substituting Eq. (13) into Eq. (12) one arrives at the following expansion of $\Xi(\alpha, \beta)$:

$$\Xi(\alpha, \beta) / \Xi_0(\alpha, \beta) = \sum_{n=0}^{\infty} (-1)^n \int_0^{\beta} dt_1 \dots \int_0^{t_{n-1}} dt_n \langle V(t_1) \dots V(t_n) \rangle \quad (15)$$

In order to use this equation we need to calculate the average $\langle V(t_1) \dots V(t_n) \rangle$ of a product of creation and destruction operators. Bloch and de Dominicis²⁰ have shown that the value of such an average may be obtained in the following way: associate the creation and destruction operators by pairs in all possible ways, then calculate for each case the product of the different pairs averaged independently, and take the sum of all such products, each one being affected by a sign which is simply (-1) exponent the number of permutations needed to bring the operators of each pair beside one another.

This rule becomes very simple to use if the different pairings are represented by diagrams in the following way (see Fig. 1): for each interaction of type v draw a dotted line; represent the creation and destruction operators by plain lines leaving and entering the two ends of the dotted line respectively; similarly with each interaction of type v' associate a wiggly line with a leaving and an entering line at one end. The n different interactions of a particular term of the average $\langle V(t_1) \dots V(t_n) \rangle$ are ordered vertically with their "time" increasing from bottom to top. The different possible pairings then correspond to the different ways of connecting two by two the lines leaving an interaction with the lines entering an interaction. The sign to be associated with a particular diagram may be shown to be $(-1)^{h+l}$, where h is the number of descending lines and l is the number of "closed loops".

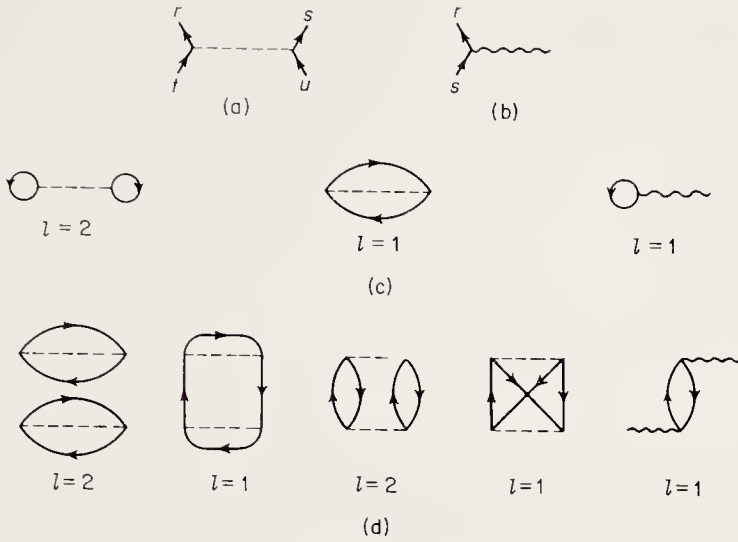


Fig. 1. Diagrammatic representations of (a) the interaction v ; (b) the interaction v' ; (c) first-order diagrams; and (d) a few second-order diagrams. All diagrams but the first of (d) are linked.

Each line will contribute the averaged product of one creation and one destruction operator. For an ascending line we have:

$$f_r^+ = \langle a_r a_r^+ \rangle = \frac{1}{1 + e^{\alpha - \beta \epsilon_r}} \quad (16)$$

and for a descending line:

$$f_r^- = \langle a_r^+ a_r \rangle = \frac{1}{1 + e^{\beta \epsilon_r - \alpha}} \quad (17)$$

A line leaving and entering the same interaction also contributes a factor f_r^- .

The most general diagram is unlinked and consists of a certain number of linked parts. A simple combinatorial calculation shows that the complete series of linked and unlinked diagrams is equal to the exponential of the series of linked diagrams only. This is essential as we are in fact interested in the logarithm of $\Xi(\alpha, \beta)$. One is then lead to the expression:

$$\ln \frac{\Xi(\alpha, \beta)}{\Xi_0(\alpha, \beta)} = \sum_{n=1}^{\infty} (-)^n \int_0^{\beta} dt_1 \dots \int_0^{t_{n-1}} dt_n \langle V(t_1) \dots V(t_n) \rangle_L \quad (18)$$

where the subscript L means that we need to take the contributions of linked diagrams only.

We still have to integrate over the ordered times. This is most simply done by the method of Laplace transforms. We shall merely state the final result:²⁰

$$A(\alpha, \beta) - A_0(\alpha, \beta) = -\frac{1}{\beta} \ln \frac{\Xi(\alpha, \beta)}{\Xi_0(\alpha, \beta)} \\ = \sum_{n=1}^{\infty} \frac{1}{O} \text{Res}_{\epsilon=0} \frac{e^{-\beta\epsilon}}{\epsilon} \left\langle V \left(\frac{1}{\epsilon - \mathcal{E}} V \right)^{n-1} \right\rangle_L \quad (19)$$

with

$$A_0(\alpha, \beta) = -\frac{1}{\beta} \ln \Xi_0(\alpha, \beta)$$

In this expression $\mathcal{E}$ represents the energy of the system between two successive interactions; more precisely if $(\epsilon - \mathcal{E})^{-1}$ is sandwiched between interactions i and $i+1$, then $\mathcal{E}_i = E_a - E_d$ where E_a and E_d are respectively the sums of the energies of the ascending lines and of the descending lines which exist in the corresponding diagram between the times t_i and t_{i+1} . The variable ϵ is complex and $\text{Res}_{\epsilon=0}$ means that one has to take the residue at the pole $\epsilon = 0$, O being the order of this pole. For example, if it so happens that for a particular diagram all energies $\mathcal{E}_i$ are different from zero, then the pole at $\epsilon = 0$ is simple and one finds:

$$(-1)^{n-1} \left\langle V \left(\frac{1}{\mathcal{E}} V \right)^{n-1} \right\rangle_L$$

Let us summarize the rules for calculating $A(\alpha, \beta) - A_0(\alpha, \beta)$:

- (a) draw all linked diagrams of all orders n ;
- (b) with each interaction associate a matrix element $\frac{1}{2} \langle rs | v | tu \rangle$ or $\langle r | v' | s \rangle$;
- (c) with each line associate a factor f_r^+ or f_r^- ;
- (d) multiply the result by

$$(-1)^{h+l} \frac{1}{O} \text{Res}_{\epsilon=0} \frac{e^{-\beta\epsilon}}{\epsilon} \prod_{i=1}^{n-1} \frac{1}{\epsilon - \mathcal{E}_i}$$

- (e) sum over the indices of the lines.

As examples let us write down the contributions of the first diagram of Fig. 1c and of the third and last diagrams of Fig. 1d:

$$(-)^{2+2} \sum_{rs} \frac{1}{2} \langle rs | v | rs \rangle f_r^- f_s^- \quad (20)$$

$$(-)^{2+2} \sum_{rstu} \left| \frac{1}{2} \langle rs | v | tu \rangle \right| \frac{2f_r^+ f_s^+ f_t^- f_u^-}{-[\epsilon_r + \epsilon_s - \epsilon_t - \epsilon_u]} \quad (21)$$

$$(-)^{1+1} \sum_{rs} |\langle r | v' | s \rangle| \frac{2f_r^+ f_s^-}{-[\epsilon_r - \epsilon_s]} \quad (22)$$

Expression (19) bears a strong resemblance to the so-called Brueckner–Goldstone perturbation series for the ground state of an N -fermion system.¹⁵ However, as was first emphasized by Kohn and Luttinger,²⁴ great care should be exercised in taking the zero temperature limit of the Bloch–de Dominicis series. Indeed, both expansions cannot become strictly identical since the Bloch–de Dominicis series corresponds to a calculation at constant activity while the Brueckner–Goldstone series corresponds to a perturbation at constant density. Furthermore, the Bloch–de Dominicis series contains “anomalous diagrams” (for instance, the second diagram of Fig. 1d), so called because they do not appear in the Brueckner–Goldstone series. In fact Luttinger and Ward²⁵ have shown that the Brueckner–Goldstone series is valid for fermions of spin $\frac{1}{2}$ only if the unperturbed Fermi sea has spherical symmetry and if the interactions are spatially isotropic. In particular, it is not valid in the presence of an external field, which is the case we are considering. The importance of these “anomalous” terms in the limit $T \rightarrow 0$ will be investigated later on (see Section IV).

B. Expansion in Powers of the Activity

To derive an expansion of the logarithm of the grand partition function in powers of the activity

$$z = e^\alpha$$

we start again from Eq. (15), which we write in the form:

$$\Xi(\alpha, \beta) = \sum_{n=0}^{\infty} (-)^n \int_0^\beta dt_1 \dots \int_0^{t_{n-1}} dt_n \text{Tr} \{ e^{-\beta H_0 + \alpha N} V(t_1) \dots V(t_n) \} \quad (23)$$

In Section II-A, we expressed the trace in terms of averages of pairs of creation and destruction operators taken over a statistical ensemble of reciprocal temperature β and activity e^z . Instead of this, we shall now relate each matrix element in the trace to the corresponding element taken over the vacuum, i.e., the state with no particles. To do this, we use the fact that any state $|\{n\}\rangle$ with N fermions in the one-particle states $m_1 \dots m_N$ may be generated from the vacuum in the following way:

$$|\{n\}\rangle = a_{m_1}^+ \dots a_{m_N}^+ |0\rangle \quad (24)$$

The trace of an operator O may therefore be written:

$$\text{Tr } O = \sum_{N=0}^{\infty} \frac{1}{N!} \sum_{m_1 \dots m_N} \langle 0 | a_{m_N} \dots a_{m_1} O a_{m_1}^+ \dots a_{m_N}^+ | 0 \rangle \quad (25)$$

where $1/N!$ corrects for the overcounting of terms in the independent summations over $m_1 \dots m_N$.

Substituting (25) into (23) we are led to evaluate the vacuum-vacuum expectation values of products of creation and destruction operators contained in $V(t)$ or introduced by the trace. We use the well-known theorem of Wick,²⁶ which expresses such an element as the sum of all possible products of "contracted" pairs of operators. This rule becomes identical with the one given in Section II-A for the evaluation of $\langle V(t_1) \dots V(t_n) \rangle$, if the statistical averages $\langle ab \rangle$ are replaced by the vacuum averages or "contractions" $\langle 0 | ab | 0 \rangle$:

$$\begin{aligned} \langle 0 | a_r a_s^+ | 0 \rangle &= \delta_{rs} \\ \langle 0 | a_s^+ a_r | 0 \rangle &= 0 \end{aligned} \quad (26)$$

As before, each term in the trace may be conveniently associated with a diagram consisting of N lines, running from bottom to top, starting from $t = 0$ in the states $m_1 \dots m_N$, then interacting with each other or with the external field and finally arriving at $t = \beta$ in the same states (see Fig. 2a). It is, in general, clearer to imagine the diagram drawn on a cylinder of circumference β . The particle lines then run around the cylinder a certain number of times before closing themselves (see Fig. 2b).

The contribution of any diagram to the series (23) is obtained in the following way:

(1) with each interaction, associate a matrix element

$$\frac{1}{2}\langle rs|v|tu\rangle \quad \text{or} \quad \langle r|v'|s\rangle$$

(2) with each particle line between two successive interactions, associate the propagator

$$\exp(-w_r \epsilon_r)$$

where ϵ_r is the energy of the line and w_r its length on the cylinder;

(3) multiply by

$$\frac{1}{N!} z^N (-1)^{n+N+l}$$

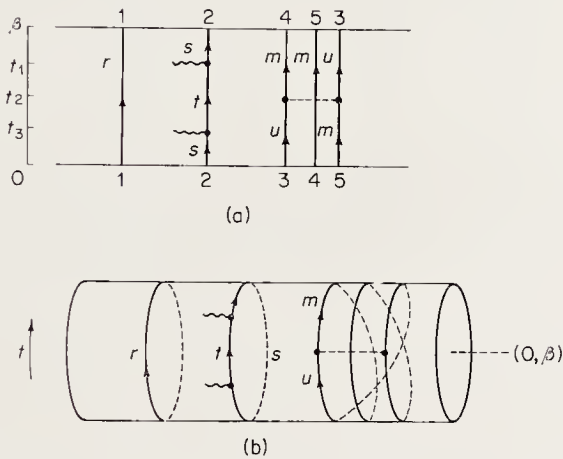


Fig. 2. Plane and cylindrical diagrammatic representations of a term in the series expansion for the grand partition function in powers of the activity ($n = 3$, $N = 5$, $l = 3$). This diagram is unlinked and consists of three linked parts.

where n is the number of interactions, N the number of particles, i.e., the number of whorls around the cylinder, and l the number of closed loops;

(4) finally, sum over the indices of the lines and integrate over the ordered times $t_1 \dots t_n$ (i.e., over the time differences w_r). As an example of these rules, we give the contribution of the diagram shown in Fig. 2:

$$(-)^{3+5+3} \frac{z^5}{5!} \int_0^\beta dt_1 \int_0^{t_1} dt_2 \int_0^{t_2} dt_3 e^{-\beta \epsilon_r} |\langle s|v'|t \rangle|^2 e^{-(t_1-t_3)\epsilon} e^{-(\beta-t_1+t_3)\epsilon_s} \frac{1}{2} \langle um|v|mu \rangle e^{-2\beta \epsilon_m} e^{-\beta \epsilon_u} \quad (27)$$

When we calculate the thermodynamic properties, we need to take the logarithm of the grand partition function. Now, in a way quite similar to that in Section II-A, a simple combinatorial

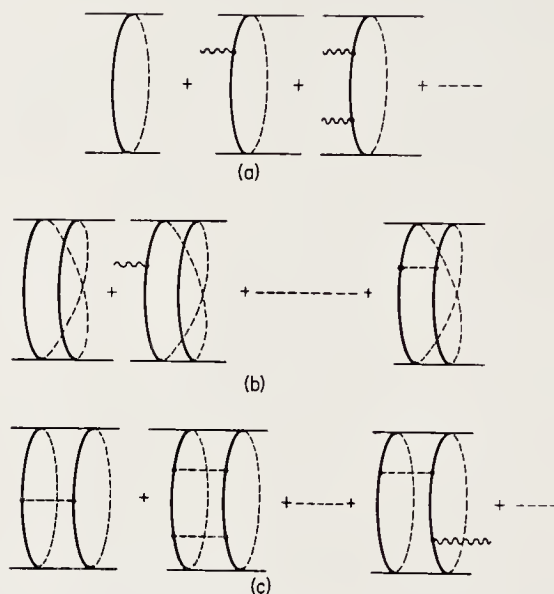


Fig. 3. (a) Diagrams contributing to B_1 ; (b) and (c) diagrams contributing to B_2 .

calculation shows that the only effect of taking the $\ln$ of the series (23) is to eliminate all unlinked diagrams. We thus arrive at:

$$\ln \Xi(\alpha, \beta) = \sum_{n=0}^{\infty} (-)^n \int_0^{\beta} dt_1 \dots \int_0^{t_{n-1}} dt_n \text{Tr} \{e^{-\beta H_0 + \alpha N} V(t_1) \dots V(t_n)\}_L \quad (28)$$

This expression may be written as a power series in z :

$$\ln \Xi(\alpha, \beta) = \sum_{l=1}^{\infty} B_l(\beta) z^l \quad (29)$$

where $B_l(\beta)$ contains the contributions of all linked diagrams with l particles. The first few diagrams for B_1 and B_2 are shown in Fig. 3.

C. Relation Between the Two Kinds of Expansion

We now proceed to show the relation between the expansions of $\Xi(\alpha, \beta)$ in powers of the interaction strength parameter (Section II-A) and in powers of the activity (Section II-B). We shall first verify that the total contribution of all linked diagrams without interactions appearing in expansion (29) is equal to $\ln \Xi_0(\alpha, \beta)$, i.e., to the logarithm of the grand partition function of the perfect Fermi gas. These diagrams consist of particle lines running around the cylinder any number N of times before closing themselves. Following the rules given in Section II-B, the contribution of such a diagram is

$$\frac{(-1)^{N+1}}{N!} \sum_r z^N e^{-N\beta\epsilon_r}$$

Multiplying this expression by the number of similar diagrams $(N-1)!$ (i.e., the number of ways of distributing N particles over a cycle) and summing over N , we find

$$-\sum_r \sum_{N=1}^{\infty} \frac{(-z e^{-\beta\epsilon_r})^N}{N} = \sum_r \ln(1 + z e^{-\beta\epsilon_r}) \equiv \ln \Xi_0(\alpha, \beta) \quad (30)$$

which is the result announced above.

We now turn to linked diagrams involving interactions. Following Bloch and de Dominicis,²¹ we shall call “spire” any particle line between two interactions if its length is greater than β , i.e., if it performs more than one whorl around the cylinder. If we start with a diagram containing any number of spires and replace these by particle lines of length smaller or equal to β , we find a similar diagram which we may call a “basic diagram”. Conversely, the whole set of diagrams containing interactions may be generated from the set of basic diagrams by replacing in all possible ways any particle line of length w by spires of length $w + k\beta$, with $k = 1, 2, \dots, \infty$. Now the effect of this insertion for a line r is to multiply the contribution of the diagram by

$$\frac{N!}{(N+k)!} (-1)^k z^k e^{-k\beta\epsilon_r}$$

Multiplying by the number of times the new diagram should be counted, $(N + k)!$, and dividing by the number of basic diagrams, $N!$, we find by summing over k :

$$\sum_{k=0}^{\infty} (-z e^{-\beta \epsilon_r})^k = \frac{1}{1 + z e^{-\beta \epsilon_r}} = f_r^+ \quad (31)$$

the statistical factor associated with ascending lines in expansion A. We have thus shown that the sum of the contributions of all diagrams corresponding to a given basic diagram is equal to the contribution of this basic diagram following the rules given in B, where the propagators $\exp(-w_r \epsilon_r)$ are replaced by

$$e^{-w_r \epsilon_r} f_r^+$$

It is then a simple matter to verify that there is a one-to-one correspondence between the basic (cylindrical) diagrams of expansion B and the (plane) diagrams of expansion A. To find the plane representation of a cylindrical diagram, one draws an ascending line for each particle line which crosses the $(0-\beta)$ axis on the cylinder and a descending line if it does not cross it. For example, the last diagram of Fig. 1d corresponds to the second linked diagram of Fig. 2. To identify completely the rules given in Sections A and B for the evaluation of these diagrams, we only need to remark that in any cylindrical diagram we may associate one factor z with each line crossing the $(0-\beta)$ axis. Such a line then contributes a factor:

$$\begin{aligned} z e^{-w_r \epsilon_r} f_r^+ &= e^{\alpha - \beta \epsilon_r} e^{(\beta - w_r) \epsilon_r} f_r^+ \\ &= e^{(\beta - w_r) \epsilon_r} f_r^- \end{aligned} \quad (32)$$

where f_r^- is the factor associated with the descending line in Section A and $(\beta - w_r)$ its length on the plane diagram.

Summarizing, we may say that in order to pass from the expansion of Section II-B to the expansion of Section II-A we simply have to perform the "summation over the spires". This will be very useful because when dealing with our particular problem we shall be able to choose, at the different stages of the calculations, the type of expansion which turns out to be the easiest one to handle.

III. ELECTRON GAS IN A LATTICE OF POSITIVE CHARGES

A. The Problem of Long-Range Forces

We shall now apply the general formalism described in Section II to the study of an electron gas in a positive medium consisting of point charges fixed on a three-dimensional periodic lattice. For the moment the exact structure of the lattice will not be specified; later on this model will be specialized to the cases of a pure metal and binary alloys.

The Hamiltonian operator for such a system may be written

$$H = -\sum_i \nabla_i^2 + U_0 + \frac{1}{2} \sum_{i \neq j} \sum v(|\mathbf{r}_i - \mathbf{r}_j|) + \sum_i v'(\mathbf{r}_i) \quad (33)$$

It only differs from Eq. (3) by the introduction of the self-energy U_0 of the positive lattice, which is actually a constant term; $v'(\mathbf{r})$ is the interaction between an electron and the whole lattice (acting as an external field) and $v(|\mathbf{r} - \mathbf{r}'|)$ is the pair-electron interaction. In order to simplify the formulae we adopt from now on the following unit system:

$$\hbar = 2m = e^2/2 = 1$$

where e is the electronic charge.* Then we have:

$$U_0 = \sum_{\alpha < \beta} \sum \frac{2\nu_{\alpha}\nu_{\beta}}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} \quad (34)$$

$$v'(\mathbf{r}) = -\sum_{\alpha} \frac{2\nu_{\alpha}}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \quad (35)$$

$$v(|\mathbf{r} - \mathbf{r}'|) = \frac{2}{|\mathbf{r} - \mathbf{r}'|} \quad (36)$$

where $\mathbf{R}_{\alpha}$ is the positional vector of the lattice site α and ν_{α} is the positive charge on this site, measured in terms of the electronic charge $|e|$.

* This system has the following advantages: (a) momentum vectors and wave vectors are numerically equal; (b) energies are expressed in Rydberg ($me^4/2\hbar^2$); and (c) distances are measured in terms of the Bohr radius ($\hbar^2/me^2$). This system of units practically coincides with the conventions used by Gell-Mann and Brueckner in their study of the ground-state energy of an electron gas.⁹

In order to apply the perturbation formalism, we now need to calculate the matrix elements of v and v' with respect to the unperturbed single-particle wave functions. These will be taken as the eigenfunctions of the momentum operator, normalized in a cubic box of volume Ω with periodic boundary conditions:

$$(1/\Omega^{\frac{1}{2}}) e^{i\mathbf{p} \cdot \mathbf{r}} \quad (37)$$

times the spin eigenfunction. The spectrum of $\mathbf{p}$ is given by:

$$\mathbf{p} = (2\pi/\Omega^{\frac{1}{2}})\mathbf{n} \quad (n_x, n_y, n_z = \text{integers}) \quad (38)$$

A one-particle state r is thus specified by the momentum $\mathbf{p}_r$ and the spin σ_r . The matrix elements of v and v' take the form:

$$\begin{aligned} \langle rs|v|tu\rangle &= \frac{1}{\Omega^2} \int \int d\mathbf{r}_1 d\mathbf{r}_2 v(|\mathbf{r}_1 - \mathbf{r}_2|) e^{i\mathbf{r}_1 \cdot (\mathbf{p}_t - \mathbf{p}_r)} e^{i\mathbf{r}_2 \cdot (\mathbf{p}_u - \mathbf{p}_s)} \\ &\quad \times \delta(\sigma_r, \sigma_t) \delta(\sigma_s, \sigma_u) \\ &= \frac{1}{\Omega} \bar{v}(|\mathbf{p}_t - \mathbf{p}_r|) \delta(\mathbf{p}_r + \mathbf{p}_s, \mathbf{p}_t + \mathbf{p}_u) \delta(\sigma_r, \sigma_t) \delta(\sigma_s, \sigma_u) \end{aligned} \quad (39)$$

where $\bar{v}(p)$ is the Fourier transform of $v(r)$:

$$\begin{aligned} \bar{v}(p) &= \int d\mathbf{r} \frac{2}{r} e^{i\mathbf{p} \cdot \mathbf{r}} \\ &= 8\pi/p^2 \end{aligned} \quad (40)$$

The matrix elements of v satisfy a momentum conservation law, owing to the spatial isotropy of v and to the spatial homogeneity of the unperturbed states. For v' , we have:

$$\begin{aligned} \langle r|v'|s\rangle &= \frac{1}{\Omega} \int d\mathbf{r} v'(\mathbf{r}) e^{i\mathbf{r} \cdot (\mathbf{p}_r - \mathbf{p}_s)} \delta(\sigma_r, \sigma_s) \\ &= \frac{1}{\Omega} \bar{v}'(\mathbf{p}_r - \mathbf{p}_s) \delta(\sigma_r, \sigma_s) \end{aligned} \quad (41)$$

with

$$\begin{aligned} \bar{v}'(\mathbf{p}) &= -\sum_{\alpha} \nu_{\alpha} \int d\mathbf{r} \frac{2}{|\mathbf{r} - \mathbf{R}_{\alpha}|} e^{i\mathbf{p} \cdot \mathbf{r}} \\ &= -\frac{8\pi}{p^2} \sum_{\alpha} \nu_{\alpha} e^{i\mathbf{p} \cdot \mathbf{R}_{\alpha}} \end{aligned} \quad (42)$$

$\bar{v}'(\mathbf{p})$ depends strongly on the lattice structure and charge distribution.

An essential difficulty of the perturbational approach to the theory of the electron gas is the appearance of divergent quantities in the expansions. This difficulty already exists in the classical case (e.g., electrolyte solutions) and has been well understood since the fundamental work of Mayer.²⁷ With regard to the quantum problem of the electron gas at zero temperature, the situation has been clarified due to the work of Bohm and Pines, Gell-Mann and Brueckner, Sawada and others.⁶⁻¹¹ The appearance of divergent integrals is evidently related to the long-range character of the electrostatic potential r^{-1} . However, the divergences may be classified into two groups of quite different origin.

The first type (I) arises from the fact that the average interaction energy between one electron and all the others varies as the integral

$$\int_{\Omega} \frac{1}{r} d\mathbf{r} \quad (43)$$

i.e., it diverges as $\Omega^{\frac{1}{2}}$ when going to the limit $\Omega \rightarrow \infty$. Such divergences are not physical ones, as one must keep the whole system electrically neutral on the average. Thus, in the case considered here, we shall impose the condition that the average number of electrons exactly neutralizes the total lattice charge. A charged particle in the system will then only feel deviation from electroneutrality around itself, attractive and repulsive interactions averaging out to zero at large distances.

The second type (II) of divergence is due to the fact that the thermodynamic properties of a plasma cannot be expressed as a series of integral powers of the interaction strength λ . For example, the ground-state energy of an electron gas contains terms proportional to $\lambda^n \ln \lambda$. It is well known that to get rid of this second type of divergence, one has to rearrange the series in such a way that the positive and negative infinities destroy each other. This is realized by summing the contributions of infinite series of diagrams before performing the various integrations.

The elimination of the divergences of type I will consist in separating them at all orders of the perturbation procedure and in grouping them into a finite result by using the macroscopic condition of electroneutrality. These divergences appear in three ways:

(1) in the lattice self-energy U_0 :

$$2\sum_{\alpha<\beta}\sum\frac{v_{\alpha}v_{\beta}}{|\mathbf{R}_{\alpha}-\mathbf{R}_{\beta}|}$$

(2) in the diagonal matrix elements of v' :

$$\langle r|v'|r\rangle = \frac{1}{\Omega} \bar{v}'(0) \equiv -\frac{2}{\Omega} (\sum_{\alpha} v_{\alpha}) \int_{\Omega} \frac{d\mathbf{r}}{r} \quad (44)$$

(3) in the diagonal matrix elements of v :

$$\langle rs|v|rs\rangle = \frac{1}{\Omega} \bar{v}(0) \equiv \frac{2}{\Omega} \int_{\Omega} \frac{d\mathbf{r}}{r} \quad (45)$$

All three types of terms involve either the integration or the summation of the electrostatic potential r^{-1} over the whole volume of the system.

It is a trivial problem to separate at the beginning of the calculations the contributions of U_0 and $\langle r|v'|r\rangle$ from the grand partition function

$$\Xi(\alpha, \beta) = \text{Tr } e^{\alpha N - \beta H} \quad (46)$$

Indeed, U_0 is a constant term which may be separated out from the start. Next, the diagonal elements of v' being independent of the index r , their contribution to the Hamiltonian is simply:

$$\sum_r \langle r|v'|r\rangle a_r^+ a_r = (N/\Omega) \bar{v}'(0) \quad (47)$$

hence we may separate them from the Hamiltonian and include them in the definition of a modified activity $\tilde{z}$:

$$\ln \tilde{z} = \tilde{\alpha} = \alpha - \beta \bar{v}'(0)/\Omega \quad (48)$$

The grand partition function then takes the form:

$$\Xi = e^{-\beta U_0} \text{Tr } e^{\tilde{\alpha}N - \beta \tilde{H}} \quad (49)$$

where

$$H = H_0 + \frac{1}{2} \sum_{rstu} \langle rs|v|tu \rangle a_r^+ a_s^+ a_u a_t + \sum_{r \neq s} \langle r|v'|s \rangle a_r^+ a_s \quad (50)$$

Unfortunately, the separation of the divergences contained in the matrix elements $\langle rs|v|rs \rangle$ cannot be accomplished from the start in such a simple manner; when we apply to expressions (49) and (50) the perturbation scheme developed in Section II, these divergences will appear at all orders. This difficulty is peculiar to the grand canonical formalism; if we had used the petit canonical ensemble,²³ such a difficulty would not have arisen, because there all terms $\langle rs|v|rs \rangle$ can be separated out of the Hamiltonian from the beginning since the total number of electrons is fixed. However, this disadvantage of the grand ensemble is largely compensated by the fact that all occupation numbers $n_r = a_r^+ a_r$ may be averaged independently (which is not the case for the petit canonical ensemble).

In the next section we shall see where divergent terms $\sim \langle rs|v|rs \rangle$ appear and show how it is possible to get rid of them by a proper rearrangement of the series expansion for Ξ .

B. Elimination of Divergences of Type I

The expression (50) for $\tilde{H}$ is of the general form (9–10); we may thus apply any of the two perturbation techniques developed in Section II to the evaluation of the partition function (49). We shall choose the expansion method in powers of the activity (Section II-B) because the elimination of divergent terms $\sim \langle rs|v|rs \rangle$ turns out to be much simpler in that case. The expression for Ξ takes the form [cf. Eq. (29)]:

$$\ln \Xi = -\beta U_0 + \sum_{l=1}^{\infty} B_l \tilde{z}^l \quad (51)$$

where the coefficient B_l is the sum of the contributions of all linked cylindrical diagrams of l particles.

Consider a particular closed loop in such a diagram. In general, a certain number of interaction lines are attached to this loop at definite points. At each such point the momentum along the loop changes discontinuously. Thus with each interaction line ending at the loop we may associate a certain momentum transferred to the loop. From the cyclic structure of the loop it follows immediately that the sum of the transferred momenta must be zero (i.e., momentum is conserved around a closed loop). Two kinds of momentum transfer are possible: (a) momentum transfer from other loops (or eventually from the same loop) with dotted lines; (b) momentum transfer from the external field, i.e., from the positive lattice (wiggly lines).

Let us number $1, 2, \dots, n, \dots$ the dotted lines and $1, 2, \dots, \nu, \dots$ the wiggly lines attached to the j th loop of a diagram and call the corresponding momentum transfers $\mathbf{p}_n^{(j)}$, $\mathbf{p}_\nu^{(j)}$. Then for this loop we have:

$$\sum_n \mathbf{p}_n^{(j)} + \sum_\nu \mathbf{p}_\nu^{(j)} = 0 \quad (52)$$

Summing over all loops of the diagram we have:

$$\sum_j \sum_n \mathbf{p}_n^{(j)} + \sum_j \sum_\nu \mathbf{p}_\nu^{(j)} = 0$$

But the first sum is clearly zero, as the momentum transferred to a loop through a dotted line is taken from another loop. Hence there remains the condition:

$$\sum_j \sum_\nu \mathbf{p}_\nu^{(j)} = 0 \quad (53)$$

meaning that the total momentum transferred to a linked diagram from the external field must be equal to zero.

Now consider a particular diagram consisting of two parts I and II linked together by a single dotted line α between two loops. Examples of such diagrams are shown in Fig. 4. It is clear from the argument given above that the total momentum transferred from the external field to part I of this diagram (through wiggly lines $1, \dots, \nu, \dots$) must be equal to the momentum $\mathbf{p}_\alpha$ transferred from part I to part II through the dotted line α :

$$\sum_I \mathbf{p}_\nu = \mathbf{p}_\alpha \quad (54)$$

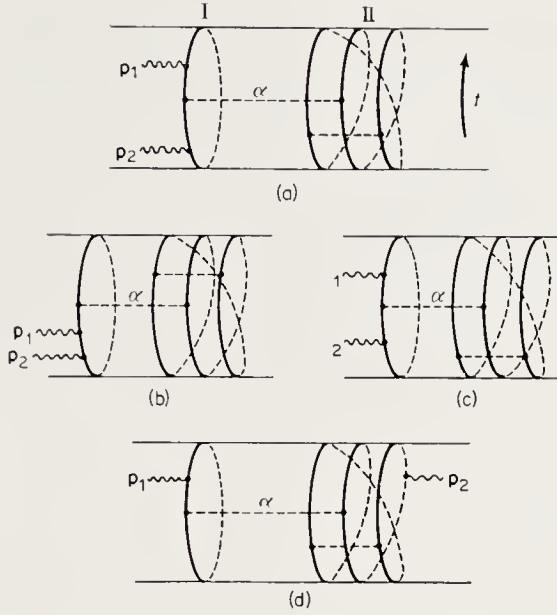


Fig. 4. Diagrams consisting of two parts linked together by a single dotted line α . (a), (b), (c) Diagrams contributing a divergent term of type I ($\mathbf{p}_1 + \mathbf{p}_2 = 0$, $\mathbf{p}_\alpha = 0$) and pertaining to the same "family of similar diagrams"; (d) diagram not contributing a divergent term of type I ($\mathbf{p}_1 + \mathbf{p}_2 = 0$, $\mathbf{p}_\alpha = \mathbf{p}_1$).

supplemented by the condition:

$$\sum_I \mathbf{p}_v = -\sum_{II} \mathbf{p}_v \quad (55)$$

on account of (53); hence $\mathbf{p}_\alpha$ is perfectly determinate. Now for diagrams such that we have separately:

$$\sum_I \mathbf{p}_v = 0 \quad \sum_{II} \mathbf{p}_v = 0 \quad (56)$$

it follows that

$$\mathbf{p}_\alpha = 0 \quad (57)$$

and the dotted line α will only contribute matrix elements of the type $\langle rs|v|rs\rangle$, i.e., those we want to separate.

Now the energies of the particle lines linked through α do not vary during this interaction, whence the associated propagators $\exp(-w_r \varepsilon_r)$ remain unchanged. Consequently, the time t_α at which α takes place only appears in the limits of the integration over the ordered times. Let us then consider the family of the diagrams

similar to the one in question, where the interaction times, in I and II separately, are ordered once and for all, but where the orders relative to each other and to t_α are changed in all possible ways (see Figs. 4b and 4c). If we take the sum of all these contributions, the integrand being identical, we only have to add up the domains of time integration. The result is then readily seen to factorize into the product of the contributions associated with parts I and II alone, times a factor γ due to the presence of the dotted line α ; more precisely, if Ξ_I and Ξ_{II} are the contributions of parts I and II alone, and Ξ_{I-II} the contribution of parts I and II connected by a line α , we have:

$$\sum_{\substack{\text{similar} \\ \text{diagrams}}} (l_I + l_{II})! \Xi_{I-II} = \gamma l_I! \Xi_I l_{II}! \Xi_{II} \quad (58)$$

where l_I , l_{II} are the number of whorls (i.e., particles) in I and II, and

$$\gamma = -\beta \bar{v}(0)/\Omega \quad (59)$$

(the factor β arising from the free integration over t_α).

This type of factorization can, of course, be extended to more complicated diagrams consisting of different parts I, II, . . ., *singly connected* by dotted lines with a zero momentum transfer. All such diagrams are *reducible* ones and may thus be expressed in terms of *irreducible* diagrams times a certain number of factors γ . This factorization procedure implies that Ξ may be expressed as a new expansion involving irreducible diagrams only, where the divergent quantity γ has been separated out at all orders. Let us define $\tilde{B}_k$ as the sum of the contributions of all *irreducible* linked diagrams of k particles. Then the first problem is to re-express the B_l 's in terms of the $\tilde{B}_k$'s; the next problem is to transform (51) into a new expansion in terms of the $\tilde{B}_k$'s.

Quite generally we may write:

$$l! B_l = \frac{1}{\gamma} \sum_{\substack{\{n_k\} \\ (\sum_k n_k = l)}} K(l, \{n_k\}) \prod_k (\gamma k! \tilde{B}_k)^{n_k} \quad (60)$$

since any reducible diagram pertaining to B_l breaks down into a set of $\{n_k\}$ subdiagrams pertaining to the $\tilde{B}_k$'s and $(\sum_k n_k - 1)$ links α , each of them contributing a factor γ ; $K(l, \{n_k\})$ is the

number of distinct ways a set of $\{n_k\}$ subdiagrams can be bound together in order to give diagrams pertaining to B_l . This combinatorial problem is very similar to the problem solved by Mayer and Harrison²⁸ in the theory of classical imperfect gases, when going from reducible cluster integrals to irreducible ones. To clarify the analogy between the two problems, let us point out that one whorl around the cylinder corresponds to a vertex in Mayer's case; here, however, two subdiagrams are connected by n interaction lines α , while in Mayer's scheme they are connected by the superposition of two vertices.

The following expression is then found for K :*

$$K(l, \{n_k\}) = l! l^{\sum_k n_k - 2} / \prod_k [(k-1)!]^{n_k} n_k! \quad (61)$$

and (60) becomes:

$$l^2 B_l = \frac{1}{\gamma} \sum_{\substack{\{n_k\} \\ (\sum_k n_k = l)}} \prod_k (\gamma l k \tilde{B}_k)^{n_k} / n_k! \quad (62)$$

This expression must now be substituted into the expressions for the grand partition function (51) and for the average number of electrons:

$$\bar{N} = \sum_{l=1}^{\infty} l B_l \tilde{z}^l \quad (63)$$

To do this it is first convenient to rewrite (62) in the form of a Cauchy integral

$$l^2 B_l = \frac{1}{\gamma} \frac{1}{2\pi i} \oint \frac{e^{l\gamma\varphi(\xi)}}{\xi^{l+1}} d\xi \quad (64)$$

around the origin (leaving all singularities other than $\xi = 0$ outside the contour), where

$$\varphi(\xi) = \sum_{k=1}^{\infty} k \tilde{B}_k \xi^k \quad (65)$$

* All whorls are distinguishable from each other at this stage.

It then follows that

$$\begin{aligned} \sum_{l=1}^{\infty} l^2 B_l \tilde{z}^{l-1} &= \frac{1}{\gamma} \frac{1}{2\pi i} \sum_{l=1}^{\infty} \oint \frac{\tilde{z}^{l-1} e^{l\gamma q(\xi)}}{\xi^{l+1}} d\xi \\ &= \frac{1}{\gamma} \frac{1}{2\pi i} \oint \frac{d\xi}{\xi(\xi e^{-\gamma q(\xi)} - \tilde{z})} \end{aligned} \quad (66)$$

with the restriction

$$|\xi e^{-\gamma q(\xi)}| > \tilde{z} \quad (67)$$

on the contour of integration. This last condition implies, from the Lagrange theorem,²⁹ that the equation

$$\xi e^{-\gamma q(\xi)} = \tilde{z} \quad (68)$$

has only one root ξ_0 inside the contour. Furthermore, as $\tilde{z}$ is a positive real number and all the $\tilde{B}_k$'s are real, ξ_0 is also real and positive. It is then found by calculating the residues of (66) at $\xi = 0$ and $\xi = \xi_0$ that:

$$\sum_{l=1}^{\infty} l^2 B_l \tilde{z}^{l-1} = \frac{1}{\gamma} \frac{d}{d\tilde{z}} \ln \left(\frac{\xi_0}{\tilde{z}} \right) \quad (69)$$

with the implicit relation:

$$\tilde{z} = \xi_0 e^{-\gamma \xi q(\xi_0)} \quad (70)$$

Integrating both sides of (69) with respect to $\tilde{z}$ we obtain [cf. Eq. (63)]:

$$\bar{N} = \sum_{l=1}^{\infty} l B_l \tilde{z}^l = \frac{1}{\gamma} \ln \left(\frac{\xi_0}{\tilde{z}} \right) \quad (71)$$

which from (70) gives:

$$\bar{N} = q(\xi_0) = \sum_{k=1}^{\infty} k \tilde{B}_k \xi_0^k \quad (72)$$

Integrating once more with respect to $\tilde{z}$, we get from (71)

$$\begin{aligned}\sum_{l=1}^{\infty} B_l \tilde{z}^l &= \int_0^{\tilde{z}} q(\xi_0) \frac{1}{\tilde{z}} d\tilde{z} \\ &= \int_0^{\xi_0} q(\xi_0) \left(\frac{1}{\xi_0} - \gamma \frac{d\varphi}{d\xi_0} \right) d\xi_0 \\ &= \sum_{k=1}^{\infty} \tilde{B}_k \xi_0^k - \frac{1}{2} \gamma \bar{N}^2\end{aligned}\quad (73)$$

This gives finally the following expression for $\Xi(\alpha, \beta)$:

$$\ln \Xi(\alpha, \beta) = -\beta U_0 - \frac{1}{2} \gamma \bar{N}^2 + \sum_{k=1}^{\infty} \tilde{B}_k \xi_0^k \quad (74)$$

We now look for the meaning of ξ_0 ; from (70) and (72) we have:

$$\xi_0 = \tilde{z} e^{\gamma \bar{N}}$$

and it follows from the definitions (48) and (59) of $\tilde{z}$ and γ that

$$\xi_0 = z \exp -\beta [\bar{N} \bar{v}(0) + \bar{v}'(0)] / \Omega \quad (75)$$

From (40) and (42) we get:

$$\bar{N} \bar{v}(0) + \bar{v}'(0) = (\bar{N} - \sum_{\alpha} \nu_{\alpha}) \int_{\Omega} \frac{2}{r} d\mathbf{r}$$

Although the Coulomb integral of the r.h.s. diverges as $\Omega^{\frac{2}{3}}$, the condition of macroscopic electroneutrality

$$\bar{N} = \sum_{\alpha} \nu_{\alpha} \quad (76)$$

ensures that this term is strictly equal to zero. Hence we have the remarkable equivalence:

$$\xi_0 = \tilde{z} \quad (77)$$

The grand partition function and the average number of electrons are then given by:

$$\ln \Xi = -\beta U_0 - \frac{1}{2} \gamma \bar{N}^2 + \sum_{k=1}^{\infty} \tilde{B}_k \tilde{z}^k \quad (78)$$

$$\bar{N} = \sum_{k=1}^{\infty} k \tilde{B}_k \tilde{z}^k \quad (79)$$

Let us now look at the quantity

$$-\beta U_0 - \frac{1}{2}\gamma\bar{N}^2$$

We have:

$$\begin{aligned} -U_0 - \frac{\gamma\bar{N}^2}{2\beta} &= -\sum_{\alpha<\beta}\sum \frac{2v_\alpha v_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} + \frac{1}{2} \frac{\bar{N}^2}{\Omega} \bar{v}(0) \\ &= \frac{\bar{N}^2}{\Omega} \int \frac{1}{r} d\mathbf{r} - \sum_{\alpha\neq\beta}\sum \frac{v_\alpha v_\beta}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \end{aligned} \quad (80)$$

where both terms diverge separately. However, on account of the electroneutrality condition (76), their difference will be finite provided that all the v_α 's are of order 1 (i.e., $\ll \bar{N}$) and that the average density of charge is the same in every macroscopic portion of the lattice.

To make this point clearer, let us consider a simple cubic lattice of spacing distance a , covered by point charges v . The electroneutrality condition is:

$$\bar{N}/\Omega = v/a^3 \quad (81)$$

and (80) becomes:

$$\frac{\bar{N}^2}{\Omega} \left\{ \int \frac{1}{r} d\mathbf{r} - a^3 \sum_{\alpha\neq 0} \frac{1}{R_\alpha} \right\} \quad (82)$$

The quantity in brackets is finite because the sum and the integral diverge in the same manner at large distances.

One should notice that if the positive lattice was replaced by a continuous background, its self-energy would become:

$$\left(\frac{\bar{N}}{\Omega}\right)^2 \iint d\mathbf{r} d\mathbf{r}' \frac{1}{|\mathbf{r} - \mathbf{r}'|} = \frac{\bar{N}^2}{\Omega} \int \frac{d\mathbf{r}}{r}$$

and U_0 would exactly cancel $-\gamma\bar{N}^2/2\beta$. This is the situation for the electron gas in a positive background. For a lattice there remains, however, the finite correction (80), which may be called a *Madelung term* because it bears a strong resemblance to the Madelung constant for ionic lattices.

We have thus achieved our end of getting rid of all divergences of type I which appeared in the original series expansion for the grand partition function. We may now proceed to evaluate the

contributions of the various irreducible linked diagrams consistently up to a given order in the coupling parameter. For this purpose it is obviously simpler to use the expansion in powers of the interaction strength described in Section II-A. As shown in Section II-C, it is very easy to pass from the expansion in powers

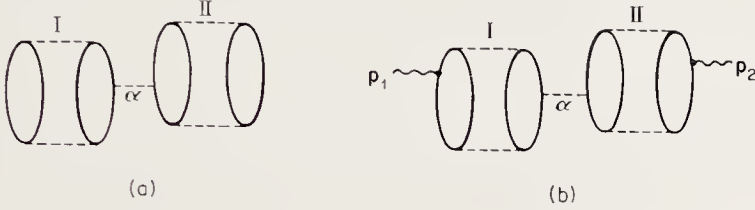


Fig. 5. Examples of linked reducible (a) and linked irreducible (b) diagrams. In (a) the momentum transferred along the dotted line α from I to II is equal to zero. In (b) it is equal to $\mathbf{p}_1 (= -\mathbf{p}_2)$.

of the activity to the expansion in powers of the coupling parameter: this is done by selecting all basic cylindrical diagrams and summing over the spires. It is then rather trivial to show from (78) that the following expression holds for $A(\alpha, \beta)$:

$$A(\alpha, \beta) = A_0(\alpha, \beta) + U_0 - \frac{1}{2}(\bar{N}^2/\Omega)\bar{v}(0) + \sum_{n=1}^{\infty} \frac{1}{O} \text{Res}_{\epsilon=0} \frac{e^{-\beta\epsilon}}{\epsilon} \left\langle V \left(\frac{1}{\epsilon - \mathcal{C}} V \right)^{n-1} \right\rangle_{L,I} \quad (83)$$

where the subscript L, I means that we are collecting linked irreducible diagrams only, i.e., diagrams which do not consist of two (or more) parts connected by a single dotted interaction line transferring no momentum from one part of the diagram to the other (see, for instance, Fig. 5).

In a similar fashion the series (79) leads to the compact expression:

$$\bar{N} = -\beta \frac{\partial}{\partial \alpha} A_0(\alpha, \beta) - \beta \frac{\partial}{\partial \alpha} \sum_{n=1}^{\infty} \frac{1}{O} \text{Res}_{\epsilon=0} \frac{e^{-\beta\epsilon}}{\epsilon} \left\langle V \left(\frac{1}{\epsilon - \mathcal{C}} V \right)^{n-1} \right\rangle_{L,I} \quad (84)$$

IV. ELECTRON GAS IN A ONE-COMPONENT LATTICE

All divergences of type I being eliminated, we now consider the particular situation of an electron gas in a "one-component lattice", i.e., in a lattice where all sites are occupied by identical point charges ν . We shall limit ourselves to the calculation of the ground-state energy. Our scheme will be the following: (1) evaluate all contributions to expansion (83) for $A(\alpha, \beta)$ at zero temperature up to a certain order in the perturbation parameter; in fact, we shall neglect all terms of order higher than the second (it is to this same degree of approximation that Gell-Mann and Brueckner⁹ calculated the ground-state energy of an electron gas in a positive background); (2) deduce from this result the expression for the ground-state energy in terms of the density; we therefore need to eliminate α between the expansions (83) and (84) for $A(\alpha, \beta)$ and $\bar{N}$.

A. Limit of Zero Temperature

The β -dependence of $A(\alpha, \beta)$ in (83) is due to the function $e^{-\beta\epsilon}$ and to the factors f^+ and f^- involved in the statistical averages. We have to consider separately the cases where the pole at $\epsilon = 0$ is simple or multiple.

When this pole is simple, i.e., all $\mathcal{E}_i$ are different from zero, the factor $e^{-\beta\epsilon}$ simply disappears when we take the residue, since

$$\text{Res}_{\epsilon=0} \frac{e^{-\beta\epsilon}}{\epsilon} \prod_i \frac{1}{(\epsilon - \mathcal{E}_i)} = \prod_i \left(\frac{-1}{\mathcal{E}_i} \right) \quad (85)$$

On the other hand, the $f^\pm$ factors are defined by Eqs. (16) and (17); we have to take their limit for $\beta \rightarrow \infty$ and $\alpha \rightarrow \infty$ in such a way that the ratio $\alpha/\beta = \epsilon_F$ remains finite, ϵ_F being the Fermi energy. These functions then reduce to step-functions:

$$f_r^- = \begin{cases} 1 & \epsilon_r < \epsilon_F \\ 0 & \epsilon_r > \epsilon_F \end{cases}, \quad f_r^+ = \begin{cases} 0 & \epsilon_r < \epsilon_F \\ 1 & \epsilon_r > \epsilon_F \end{cases} \quad (86)$$

and their role is to limit the summations over the states located inside and outside the Fermi sphere respectively.

Let us now see what happens when the pole at $\epsilon = 0$ is multiple. Of this situation we shall encounter only one example in our calculations: that of the second diagram of Fig. 1d. Its contribution to $A(\alpha, \beta)$ is the following:

$$(-1)^{1+3} \sum_{rstu} \frac{1}{4} \langle rs|v|st \rangle \langle tu|v|ur \rangle f_r^+ f_s^- f_t^- f_u^- \frac{1}{O} \text{Res}_{\epsilon=0} \frac{e^{-\beta\epsilon}}{\epsilon} \frac{1}{\epsilon - \epsilon_r + \epsilon_t} \quad (87)$$

From the total momentum conservation in the v interactions, it follows that the states r and t must be the same. Hence the pole at $\epsilon = 0$ is a double one and the residue

$$\text{Res}_{\epsilon=0} (e^{-\beta\epsilon}/\epsilon^2) = -\beta \quad (88)$$

becomes infinite for $\beta \rightarrow \infty$. On the other hand, as $\epsilon_r = \epsilon_t$, Eq. (87) contains the product $f_r^+ f_r^-$, which is zero everywhere except at $\epsilon_r = \epsilon_F$ in the limit $\beta \rightarrow \infty$. The product $\beta f_r^+ f_r^-$, however, has a well defined behavior in this limit; indeed, as

$$\beta f_r^+ f_r^- = \beta \frac{e^{\alpha - \beta\epsilon_r}}{(1 + e^{\alpha - \beta\epsilon_r})^2} = \frac{d}{d\epsilon_r} f_r^+ \quad (89)$$

it tends to a delta-function $\delta(\epsilon_r - \epsilon_F)$ when $\beta \rightarrow \infty$. As a general rule, every time the pole at $\epsilon = 0$ is multiple, a certain number of β factors appear in the calculation of the residue which must be combined with products $f_r^+ f_r^-$ to form either delta-functions, $\delta(\epsilon_r - \epsilon_F)$, or derivatives, $\delta'(\epsilon_r - \epsilon_F)$, . . . , in the limit $\beta \rightarrow \infty$. The corresponding diagrams are the so-called "anomalous" ones already mentioned in Section II-A. Their physical meaning will be discussed in Section IV-C.

B. Evaluation of the Diagrams

Let us first establish the particular expression for the matrix elements $\langle r|v'|s \rangle$ for the case of a "one-component" lattice. From the general expression (42) we have:

$$\tilde{v}'(\mathbf{p}) = -\frac{8\pi\nu}{p^2} \sum_{\alpha} e^{i\mathbf{p} \cdot \mathbf{R}_{\alpha}} \quad (90)$$

Using the well-known relation

$$\sum_{\alpha} e^{i\mathbf{p} \cdot \mathbf{R}_{\alpha}} = L \sum_{\mathbf{k}} \delta(\mathbf{p}, \mathbf{k}) \quad (91)$$

where L is the total number of lattice sites and $\mathbf{k}$ is a vector of the reciprocal lattice,* we obtain:

$$\bar{v}'(\mathbf{p}) = -\frac{8\pi\nu}{p^2} L \sum_{\mathbf{k}} \delta(\mathbf{p}, \mathbf{k})$$

and from (41):

$$\langle r|v'|s\rangle = \delta(\sigma_r, \sigma_s) \sum_{\mathbf{k}} c_{\mathbf{k}} \delta(\mathbf{p}_r - \mathbf{p}_s, \mathbf{k}) \quad (92)$$

with

$$c_{\mathbf{k}} = -\frac{\nu s}{v_0} \frac{8\pi}{k^2} \quad (93)$$

In this expression v_0 is the volume of the unit cell and s is the number of sites per cell. For instance, in the case of a body-centered lattice, s equals 2 and $v_0 = a^3$ is the volume of a cubic cell of side a with a lattice site at its center; the vectors $\mathbf{k}$ form a face-centered cubic lattice with lattice distance $4\pi/a$.† We shall in fact limit ourselves to the consideration of the three cubic lattices.

Let us now proceed to calculate the various contributions to the expression (83) for $A(\alpha, \beta)$ in the limit of zero temperature. We define:

$$\lim_{\substack{\beta \rightarrow \infty \\ (\alpha/\beta = \epsilon_F)}} A(\alpha, \beta) = A(\epsilon_F) \quad (94)$$

and similarly

$$\lim_{\substack{\beta \rightarrow \infty \\ (\alpha/\beta = \epsilon_F)}} A_0(\alpha, \beta) = A_0(\epsilon_F) \quad (94')$$

* The reciprocal lattice is defined by the following relations between its basic vectors $(\mathbf{k}_1, \mathbf{k}_2, \mathbf{k}_3)$ and those of the original lattice $(\mathbf{R}_1, \mathbf{R}_2, \mathbf{R}_3)$:

$$\mathbf{R}_i \cdot \mathbf{k}_j = 2\pi \delta_{ij}$$

† It is clear that the appearance in Eq. (92) of vectors of the reciprocal lattice only is a direct consequence of the fact that $v'(\mathbf{r})$ is a space-periodic function with Fourier components $c_{\mathbf{k}}$.

A careful investigation shows that the only terms of order $\leq O(\lambda^2)$ are the following ones.

(1) *Zeroth Order*

The unperturbed term $A_0(\epsilon_F)$ is equal to

$$A_0(\epsilon_F) = -(2/15\pi^2)\Omega\epsilon_F^{\frac{5}{2}} \quad (95)$$

(perfect gas of fermions with spin $\frac{1}{2}$).

(2) *Madelung Term*

It is equal to [cf. Eq. (80)]:

$$\begin{aligned} A_{\text{Mad}} &= U_0 - \frac{1}{2} \frac{\bar{N}^2}{\Omega} v(0) \\ &= L\nu^2 \sum_{\alpha \neq 0} \frac{1}{R_\alpha} - \frac{\bar{N}^2}{\Omega} \int \frac{1}{r} d\mathbf{r} \\ &= -\frac{\bar{N}^2}{\Omega} \left\{ \int \frac{1}{r} d\mathbf{r} - \frac{a^3}{s} \sum_{\alpha \neq 0} \frac{1}{R_\alpha} \right\} \end{aligned} \quad (96)$$

where we have used the fact that the system is electrically neutral:

$$\bar{N} = L\nu = \Omega s\nu/a^3 \quad (97)$$

Defining the pure numbers:

$$\tilde{r} = r/a \quad \tilde{R}_\alpha = R_\alpha/a$$

we may rewrite the Madelung term in the form:

$$A_{\text{Mad}} = -\frac{\bar{N}^2}{\Omega} a^2 \chi = -\bar{N} \left(\frac{\bar{N}}{\Omega} \right)^{\frac{1}{3}} (s\nu)^{\frac{2}{3}} \chi \quad (98)$$

where

$$\chi = \int \frac{1}{\tilde{r}} d\tilde{\mathbf{r}} - \frac{1}{s} \sum_{\alpha \neq 0} \frac{1}{\tilde{R}_\alpha} \quad (99)$$

is a numerical constant depending on the type of lattice considered. The values of χ are given in Table I for the three cubic lattices.

TABLE I. Values of the Constant χ^a

Lattice	s	χ
s.c.	1	2.83730
b.c.	2	1.81962
f.c.c.	4	1.14622

^a These values of χ have been calculated by transforming Eq. (99) into a rapidly converging series.³⁰

(3) First Order

The first-order diagrams are drawn in Fig. 1c. Now the first of these is reducible and must no longer be counted. The third diagram also disappears because the momentum transferred from the lattice field is necessarily zero and the corresponding matrix elements $\langle r|v'|r\rangle$ have been separated out at the start (cf. Section III-A).

There remains only the second diagram, which is known as the "exchange term". Following the rules given in Section II-A its contribution to $A(\alpha, \beta)$ is:

$$-\sum_r \sum_s \frac{1}{2} \langle rs|v|sr\rangle f_r^- f_s^- \quad (100)$$

where the index r represents both the momentum $\mathbf{p}_r$ and the spin σ_r . Replacing the matrix element by its value (39) we obtain:

$$-\frac{1}{2\Omega} \sum_{\sigma_r} \sum_{\mathbf{p}_r} \sum_{\sigma_s} \sum_{\mathbf{p}_s} \frac{8\pi}{|\mathbf{p}_r - \mathbf{p}_s|^2} \delta(\sigma_r, \sigma_s) f_r^- f_s^- \quad (101)$$

In the limit $\Omega \rightarrow \infty$, we may replace the sums over $\mathbf{p}$ by integrals:

$$\sum_{\mathbf{p}} \rightarrow \frac{\Omega}{8\pi^3} \int d\mathbf{p} \quad (102)$$

Summing over the spin states and passing to the limit of zero temperature, we get from (101) the following contribution to $A(\epsilon_F)$:

$$A_{\text{ex}}(\epsilon_F) = -\frac{\Omega}{8\pi^5} \int_{p_r < P} d\mathbf{p}_r \int_{p_s < P} d\mathbf{p}_s \frac{1}{|\mathbf{p}_r - \mathbf{p}_s|^2} \quad (103)$$

where $P = \epsilon_F^{\frac{1}{2}}$ is the radius of the Fermi sphere; the integrations are readily performed with the result:

$$A_{\text{ex}}(\epsilon_F) = -\frac{\Omega}{2\pi^3} \epsilon_F^2 \quad (104)$$

(4) Second Order

We need to take into account the four linked diagrams given in Fig. 1d. Let us first consider the third and the fourth of these diagrams, which are reproduced in Figs. 6a and 6b. For (a) we have the contribution:

$$2 \sum_{rstu} \frac{1}{4} |\langle rs | v | tu \rangle| 2f_t^+ f_u^+ f_r^- f_s^- \frac{1}{-[\dot{p}_t^2 + \dot{p}_u^2 - \dot{p}_r^2 - \dot{p}_s^2]} \quad (105)$$

(simple pole in $\varepsilon = 0$). The factor 2 in front takes account of the fact that there are two diagrams of this type. Replacing the matrix elements by their values we obtain:

$$-\frac{1}{2\Omega^2} \sum_{\substack{\sigma_r \sigma_s \\ \sigma_t \sigma_u}} \delta(\sigma_r, \sigma_t) \delta(\sigma_s, \sigma_u) \sum_{\substack{\mathbf{p}_r \mathbf{p}_s \\ \mathbf{p}_t \mathbf{p}_u}} \left(\frac{8\pi}{|\mathbf{p}_t - \mathbf{p}_r|^2} \right)^2 \delta(\mathbf{p}_r + \mathbf{p}_s, \mathbf{p}_t + \mathbf{p}_u) \\ f_t^+ f_u^+ f_r^- f_s^- \frac{1}{\dot{p}_t^2 + \dot{p}_u^2 - \dot{p}_r^2 - \dot{p}_s^2} \quad (106)$$

This finally gives in the limit $\Omega \rightarrow \infty, \beta \rightarrow \infty$:

$$-\frac{\Omega}{8\pi^7} \int_{p_r < P, p_s < P, |\mathbf{p}_r + \mathbf{q}| > P, |\mathbf{p}_s - \mathbf{q}| > P} d\mathbf{p}_r d\mathbf{p}_s d\mathbf{q} \frac{1}{q^4} \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{p}_r - \mathbf{p}_s)} \quad (107)$$

Now this integral diverges for $q \rightarrow 0$ and is an example of a divergence of type II as introduced in Section III-A. The way to overcome this difficulty is well known: we have to look for similar divergences in higher-order diagrams and sum an infinite series of them. It may easily be shown that the family of diagrams

needed here are the closed ring diagrams, of which the first few terms are represented in Figs. 6a, c, d, d', and d". There is a one-to-one correspondence between these diagrams and the diagrams considered by Gell-Mann and Brueckner⁹ for the electron gas in a positive continuum.

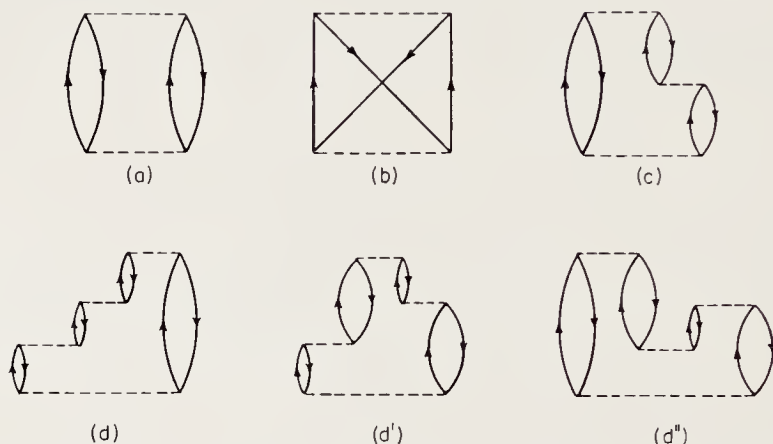


Fig. 6. Second, third, and fourth-order diagrams of the family summed by Gell-Mann and Brueckner.

The diagram of Fig. 6b is finite and its contribution is easily identified with the finite second-order exchange term included by Gell-Mann and Brueckner:⁹

$$\frac{\Omega}{16\pi^7} \int_{\substack{p_r < P, p_s < P \\ |\mathbf{p}_r + \mathbf{q}| > P, |\mathbf{p}_s - \mathbf{q}| > P}} d\mathbf{p}_r d\mathbf{p}_s d\mathbf{q} \frac{1}{q^2} \frac{1}{|\mathbf{p}_r + \mathbf{q} - \mathbf{p}_s|^2} \frac{1}{q^2 + \mathbf{q} \cdot (\mathbf{p}_r - \mathbf{p}_s)} \quad (108)$$

The sum of all the ring diagrams plus the exchange second-order term has been computed by Gell-Mann and Brueckner; its contribution to $A(\alpha, \beta)$ is

$$A_{\text{ring}}(\epsilon_F) = (\Omega/3\pi^2) \epsilon_F^{\frac{3}{2}} [0.0622 \ln(9\pi/4)^{\frac{1}{2}} \epsilon_F^{-\frac{1}{2}} - 0.096] + \Omega O(\epsilon_F \ln \epsilon_F^{-\frac{1}{2}}) \quad (109)$$

One may verify that the dependence of A_{ring} upon the interaction strength λ is of the form:

$$A_{\text{ring}}(\epsilon_F) \sim \lambda^2(a \ln \lambda + b) + O(\lambda^3 \ln \lambda) \quad (109')$$

(λ being proportional to e^2). The appearance of a logarithmic term in (109') precludes a McLaurin expansion of the ground-state energy in powers of λ ; this is the origin of the divergences we met in isolated diagrams.

We now proceed to the evaluation of the second diagram of Fig. 1d. This is precisely the anomalous term examined in Section IV-A [cf. Eqs. (87), (88), and (89)]. In the limit of zero temperature its contribution is

$$\begin{aligned}
 A_{\text{an}}(\epsilon_F) &= -\frac{\Omega}{8\pi^7} \int_{p_u < P, p_s < P} d\mathbf{p}_r d\mathbf{p}_s d\mathbf{p}_u \frac{1}{|\mathbf{p}_r - \mathbf{p}_s|^2} \frac{1}{|\mathbf{p}_r - \mathbf{p}_u|^2} \delta(p_r^2 - P^2) \\
 &= -\frac{\Omega}{\pi^4} \epsilon_F^3
 \end{aligned} \tag{110}$$

[This expression includes a factor 4 because this diagram appears four times in the expansion of $\Xi(\alpha, \beta)$.]

The contribution of the last diagram of Fig. 1d, which takes account of the *polarization* of the electron gas by the positive lattice, remains to be calculated. According to the rules of Section II-A, the contribution of this diagram is equal to

$$\sum_{\sigma_r \sigma_s} \sum_{\mathbf{p}_r \neq \mathbf{p}_s} \langle r|v'|s \rangle \langle s|v'|r \rangle f_r^+ f_s^- \frac{1}{-[\epsilon_r - \epsilon_s]}$$

(where the matrix elements diagonal in $\mathbf{p}$ have been excluded). Using Eq. (92) for $\langle r|v'|s \rangle$, we arrive at

$$\begin{aligned}
 & - \sum_{\sigma_r \sigma_s} \delta(\sigma_r, \sigma_s) \sum_{\mathbf{p}_r \neq \mathbf{p}_s} f_r^+ f_s^- \frac{1}{p_r^2 - p_s^2} \\
 & \quad \sum_{\mathbf{k}_1} c_{\mathbf{k}_1} \delta(\mathbf{p}_r - \mathbf{p}_s, \mathbf{k}_1) \sum_{\mathbf{k}_2} c_{\mathbf{k}_2} \delta(\mathbf{p}_s - \mathbf{p}_r, \mathbf{k}_2)
 \end{aligned}$$

This finally gives in the limit $\Omega \rightarrow \infty, \beta \rightarrow \infty$:

$$A_{\text{pol}}(\epsilon_F) = -\frac{\Omega}{4\pi^3} \sum_{\mathbf{k} \neq 0} c_{\mathbf{k}} c_{-\mathbf{k}} \int_{\substack{p < P \\ |\mathbf{p} + \mathbf{k}| > P}} d\mathbf{p} \frac{1}{|\mathbf{p} + \mathbf{k}|^2 - p^2} \tag{111}$$

The limits of integration lead us to consider separately the situations where k is greater or smaller than $2P$ (see Fig. 7).

For $k > 2P$, we must integrate over $\mathbf{p}$ inside the whole Fermi sphere and the denominator

$$|\mathbf{p} + \mathbf{k}|^2 - p^2$$

never vanishes. For $k < 2P$, the integration is restricted to the shaded domain of Fig. 7 (II); on the circumference indicated by arrows one has

$$|\mathbf{p} + \mathbf{k}| = p$$

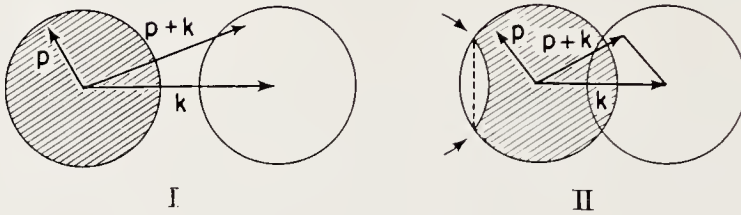


Fig. 7. Domains of integration over $\mathbf{p}$ in Eq. (111). Case I: $k > 2P$. Case II: $k < 2P$. The arrows in II indicate the position of the circumference where $p = |\mathbf{p} + \mathbf{k}|$.

so that the integrand of (111) becomes infinite. Actually this divergence is not strong enough to lead to a divergence in the integral itself. However, it may be shown that for higher-order diagrams where a particle interacts several times with the same component $c_{\mathbf{k}}$ of the lattice field, the corresponding integral diverges. Now $\mathbf{k}$ is a vector of the reciprocal lattice and when $k < 2P$, the Fermi sphere cuts the surface of a particular Brillouin zone; hence the divergences mentioned above are clearly related to a "band effect" which cannot be treated by the usual perturbation method. Once again one should look for an infinite series of diverging terms and sum them before integrating over $\mathbf{p}$. However, when this is done, one finds that beyond the second-order finite term (111), the first "band effect" correction is of order three (i.e., proportional to $\lambda^3 \sim e^6$). Thus, we do not need to take

it into account here. We therefore limit ourselves to expression (111), which gives after integration:

$$A_{\text{pol}}(\epsilon_F) = -\frac{\Omega}{8\pi^2} \epsilon_F^{\frac{3}{2}} \sum_{\mathbf{k} \neq 0} c_{\mathbf{k}} c_{-\mathbf{k}} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \quad (112)$$

with

$$\mathbf{u} = \mathbf{k}/2\epsilon_F^{\frac{1}{2}} \quad (113)$$

Replacing $c_{\mathbf{k}}$ by its value in terms of $\mathbf{u}$,

$$c_{\mathbf{k}} = -\frac{\nu s}{v_0} \frac{8\pi}{k^2} = -\frac{2\pi\nu s}{\epsilon_F v_0} \frac{1}{u^2} \quad (114)$$

and eliminating v_0 through the condition of electroneutrality

$$\bar{N} = \Omega\nu s/v_0 \quad (115)$$

we finally obtain:

$$A_{\text{pol}}(\epsilon_F) = -\frac{1}{2} \frac{\bar{N}^2}{\Omega} \epsilon_F^{-\frac{3}{2}} \sum_{\mathbf{u} \neq 0} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \quad (116)$$

$\mathbf{u}$ is of the form:

$$\mathbf{u} = \left(\frac{\pi}{3\nu s} \right)^{\frac{1}{2}} \mathbf{n} \quad (117)$$

and n_x, n_y, n_z are integral numbers; the sum over $\mathbf{u}$ in Eq. (116) involves all points of the reciprocal lattice. Some values of this sum are quoted in Table II for the three cubic lattices.

TABLE II. Numerical Values of the Sum:

$$\sum_{\mathbf{u} \neq 0} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\}$$

for Various Cubic Lattices. $[\mathbf{u} = (\pi/3\nu s)^{\frac{1}{2}} \mathbf{n}]$

Lattice	s	ν	
s.c.	1	1	6.8203
		2	28.10
b.c.	2	1	5.3192
f.c.c.	4	1	5.3654

To summarize, the value of $A(\epsilon_F)$ up to the second order in the interaction strength λ is given by the sum

$$A(\epsilon_F) = A_0(\epsilon_F) + A_{\text{Mad}} + A_{\text{ex}}(\epsilon_F) \\ + A_{\text{ring}}(\epsilon_F) + A_{\text{an}}(\epsilon_F) + A_{\text{pol}}(\epsilon_F) \quad (118)$$

On the other hand, the average number of electrons is given by

$$\bar{N} = -\frac{\partial}{\partial \epsilon_F} \{A_0(\epsilon_F) + A_{\text{ex}}(\epsilon_F) + A_{\text{ring}}(\epsilon_F) \\ + A_{\text{an}}(\epsilon_F) + A_{\text{pol}}(\epsilon_F)\} \quad (119)$$

on account of Eq. (84).

C. Ground-State Energy in Terms of the Density

The ground-state energy E^0 of the system may be obtained from the limiting value of the free energy:

$$\lim_{\beta \rightarrow \infty} F = E^0$$

hence from Eq. (6) we have:

$$E^0 = \bar{N}\epsilon_F + A(\epsilon_F) \quad (120)$$

We now want to express E^0 in terms of the density $\bar{N}/\Omega$; this means that we have to eliminate ϵ_F between (120) and (119).

Let ϵ_F^0 be the Fermi energy of a free-electron gas at the same density $\bar{N}/\Omega$ as the perturbed system:

$$\bar{N} = -\frac{\partial}{\partial \epsilon_F^0} A_0(\epsilon_F^0) \quad (121)$$

The difference $(\epsilon_F - \epsilon_F^0)$ is clearly related to the electrostatic interactions and will be at least of the first order in the interaction strength λ . Expanding (120) around ϵ_F^0 , we have:

$$E^0 = \bar{N}\epsilon_F^0 + A(\epsilon_F^0) + \left\{ \bar{N} + \frac{\partial}{\partial \epsilon_F^0} A(\epsilon_F^0) \right\} \delta\epsilon \\ + \frac{1}{2} \frac{\partial^2}{\partial \epsilon_F^2} A(\epsilon_F^0) (\delta\epsilon)^2$$

up to second-order terms in $\delta\epsilon = \epsilon_F - \epsilon_F^0$. Retaining only second-order terms in the interaction strength and taking account of (121), we still have:

$$E^0 = \bar{N}\epsilon_F^0 + A(\epsilon_F^0) + \frac{\partial}{\partial\epsilon_F^0} A_{\text{ex}}(\epsilon_F^0) \delta\epsilon + \frac{1}{2} \frac{\partial^2}{\partial\epsilon_F^{02}} A_0(\epsilon_F^0) (\delta\epsilon)^2 \quad (122)$$

Now the value of $\delta\epsilon$ to the first order in λ may be obtained from the expansion of (119):

$$\bar{N} = -\frac{\partial}{\partial\epsilon_F^0} A_0(\epsilon_F^0) - \frac{\partial}{\partial\epsilon_F^0} A_{\text{ex}}(\epsilon_F^0) - \frac{\partial^2}{\partial\epsilon_F^{02}} A_0(\epsilon_F^0) \delta\epsilon \quad (123)$$

which gives on account of (121):

$$\delta\epsilon = -\frac{\partial}{\partial\epsilon_F^0} A_{\text{ex}}(\epsilon_F^0) \bigg/ \frac{\partial^2}{\partial\epsilon_F^{02}} A_0(\epsilon_F^0) \quad (124)$$

Hence the expression for E^0 is

$$E^0 = \bar{N}\epsilon_F^0 + A(\epsilon_F^0) - \frac{1}{2} \left\{ \frac{\partial}{\partial\epsilon_F^0} A_{\text{ex}}(\epsilon_F^0) \right\}^2 \bigg/ \frac{\partial^2}{\partial\epsilon_F^{02}} A_0(\epsilon_F^0) \quad (125)$$

It is then easily verified from (95), (104), and (110) that we have the remarkable equality:

$$A_{\text{an}}(\epsilon_F^0) = \frac{1}{2} \left\{ \frac{\partial}{\partial\epsilon_F^0} A_{\text{ex}}(\epsilon_F^0) \right\}^2 \bigg/ \frac{\partial^2}{\partial\epsilon_F^{02}} A_0(\epsilon_F^0) \quad (126)$$

Thus the anomalous term exactly compensates the correction introduced in going from ϵ_F^0 to ϵ_F . This fact was first recognized by Kohn and Luttinger.²⁴ Later on, Luttinger and Ward²⁵ showed that this compensation takes place at all orders, if the unperturbed Fermi sea has spherical symmetry and if the interactions are isotropic. They established in this way the correctness of the Brueckner–Goldstone perturbation formula under these special conditions. Here, however, as the electron–lattice interaction $v'(\mathbf{r})$ is not isotropic, it is clear that such a compensation will not occur at all orders; in fact it happens accidentally for second-order terms. We thus have:

$$\begin{aligned} E^0 &= \bar{N}\epsilon_F^0 + A(\epsilon_F^0) - A_{\text{an}}(\epsilon_F^0) \\ &= \bar{N}\epsilon_F^0 + A_0(\epsilon_F^0) + A_{\text{Mad}} + A_{\text{ex}}(\epsilon_F^0) \\ &\quad + A_{\text{ring}}(\epsilon_F^0) + A_{\text{pol}}(\epsilon_F^0) \end{aligned} \quad (127)$$

It is now easy to replace the chemical potential ϵ_F^0 by the density of the system; indeed from (121) and (95) we have:

$$\bar{N} = (\Omega/3\pi^2)\epsilon_F^{0\frac{3}{2}} \quad (128)$$

In terms of the variable r_s introduced by Wigner through the relation

$$(\bar{N}/\Omega)^{-1} = (4\pi/3)r_s^3 \quad (129)$$

(which is a measure of the average distance between two electrons), the ground-state energy per electron takes the following form:

$$\begin{aligned} \epsilon(r_s) = \frac{E^0}{\bar{N}} = & \frac{3}{5} \left(\frac{9\pi}{4} \right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{1}{3} \left(\frac{3s\nu}{\pi} \right)^{\frac{2}{3}} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \chi \frac{1}{r_s} - \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{1}{r_s} \\ & + 0.0622 \ln r_s - 0.096 - \frac{1}{6\pi^2} \sum_{u \neq 0} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \\ & + O(r_s \ln r_s) \end{aligned} \quad (130)$$

In this expression, the physical meaning of the various terms is the following:

- (a) the first term is the kinetic energy of a free-electron gas;
- (b) the second term is the Madelung energy [see Eq. (98)] of a lattice of positive point charges in a uniform negative background;
- (c) the third term is the exchange energy of the electron gas, as calculated by Wigner;⁴
- (d) the fourth term is the correlation energy of the electron gas, as calculated by Gell-Mann and Brueckner;⁹ and
- (e) the fifth term is the polarization energy of the free-electron gas by the lattice, in the linear approximation.

The sum of terms (a), (c), and (d) is just the ground-state energy of an electron gas in a positive continuum; terms (b) and (e) arise from the lattice.

D. Discussion of the Results

Expression (130) is plotted in Fig. 8 (curve I) for the special case of a simple cubic lattice with $\nu = 1$. The importance of the "structural" terms (b) and (e) is apparent when one compares curve I with curve II, the latter corresponding to an electron gas in a uniform positive background. For body-centered and face-centered cubic lattices, curves very similar to curve I are obtained.

For $\nu = 1$, our model corresponds very closely to a metallic form of solid hydrogen. The ground-state energy of metallic hydrogen has been investigated by Wigner and Huntington;³ they first looked for approximate Bloch wave functions for independent electrons and next calculated exchange and correlation corrections. This method of approach is rather different

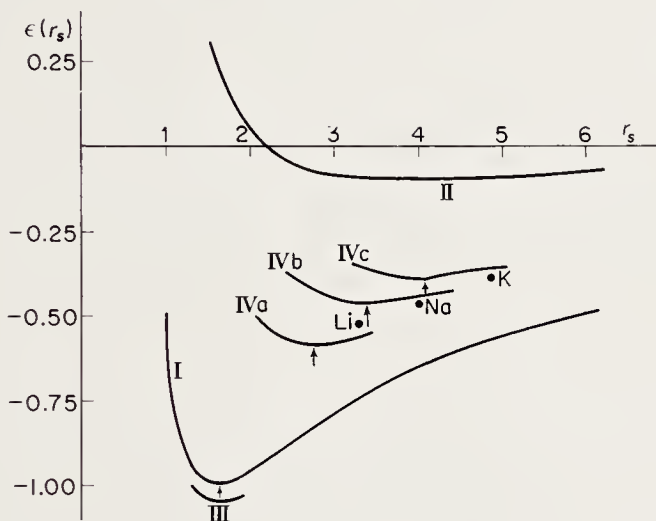


Fig. 8. Ground-state energy (per electron) in terms of r_s .
 Curve I: Eq. (130) with $\nu = 1$, $s = 1$ (simple cubic lattice).
 Curve II: electron gas in a positive continuum (Gell-Mann and Brueckner).
 Curve III: calculations of Wigner and Huntington.³
 Curves IVa, IVb, and IVc: modified Coulomb potential, Eq. (140) with $\nu = 1$, $s = 1$, and $r_0 = 1.0, 1.5$, and 2.0 respectively.
 •: experimental points for actual metals.

from ours, which treats electron-electron and electron-lattice interactions in a symmetric way. It is then quite remarkable that the curve III for $\epsilon(r_s)$ derived by Wigner and Huntington is very close to our curve I, as can be seen from Fig. 8. The abscissae and ordinates at the minimum are, respectively: $r_s = 1.64$, $\epsilon(r_s) = -1.05$, and $r_s = 1.59$, $\epsilon(r_s) = -0.99$. We may further expect that the exact minimum value of $\epsilon(r_s)$ for metallic hydrogen is somewhat below -1 Rydberg. This indicates that expansions for $\epsilon(r_s)$ such as (130) converge satisfactorily in the region $r_s < 2$. This also seems to be supported by the calculations of Dubois¹²⁻¹³

for the term $O(r_s \ln r_s)$ of the correlation energy of an electron gas in a uniform positive background, and also by our own estimate of the polarization energy $O(r_s)$ of the electrons in the lattice.

The experimental points corresponding to the series of the alkali metals have also been included in Fig. 8* (these metals correspond to $\nu = 1$). It is at once clear that our model cannot

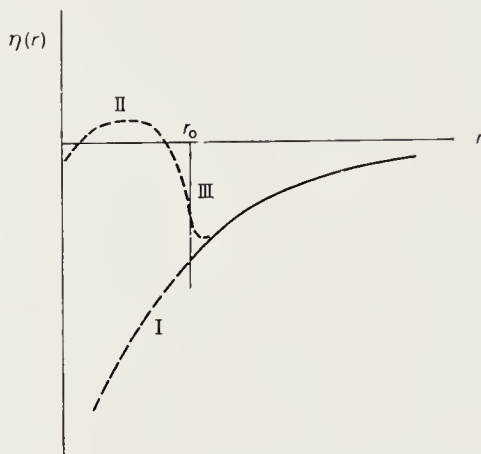


Fig. 9. Interaction of a nearly free electron with an ion of the lattice.

Curve I: Coulomb potential for a point ion.

Curve II: schematic behavior of the true interaction following Cohen and Heine.³⁴

Curve III: Coulomb potential with a cut-off at short distances.

be considered as an adequate picture of these solids. This is essentially due to the fact that we neglected the exact structure of the ions and represented them by point charges. To improve the agreement between our results and experiment, we need a better approximation for the effective interaction potential between the nearly free electrons and the ion cores.

Indeed, what is clearly missing in our model is a specific parameter taking account of the nature of the metal under consideration. This problem has been investigated by different authors.³¹⁻³⁴

* In terms of experimental quantities, the value of $\epsilon(r_s)$ at the minimum corresponds to

$$-(\Delta H_{\text{vap}} + I)$$

where ΔH_{vap} is the enthalpy of vaporization and I the first ionization potential for the free atom.

In particular, Cohen and Heine have shown that the average potential to which nearly free electrons are submitted cancels out at short distances due to interactions with bound electrons surrounding the nucleus (see Fig. 9). They suggested, therefore, that a reasonable approximation for the electron-ion interaction would be

$$\eta(r) = \begin{cases} -2\nu/r & r > r_0 \\ 0 & r < r_0 \end{cases} \quad (131)$$

i.e., a Coulomb potential with a cut-off at short distances. This introduces into the model a semiempirical parameter r_0 which relates to the specific nature of the metal under consideration. In the next section we shall discuss the influence of such a refinement upon the ground-state energy.

E. Effect of the Structure of the Positive Charges. Modified Coulomb Potential

We now calculate the ground-state energy of an electron gas interacting with the lattice charges through the modified Coulomb potential (131). The calculations follow the same steps as for the case of point charges. We shall therefore merely state the points at which differences must be introduced. This, of course, only happens in the contributions where the lattice plays some role, i.e., the Madelung term and the polarization term.

The interaction energy between an electron and the whole lattice takes the form:

$$v'(\mathbf{r}) = -2\nu \sum_{\alpha} \frac{1}{|\mathbf{r} - \mathbf{R}_\alpha|} \quad (132)$$

($|\mathbf{r} - \mathbf{R}_\alpha| > r_0$)

where the sum is now restricted to the sites α such that the distance $|\mathbf{r} - \mathbf{R}_\alpha|$ is larger than r_0 . On physical grounds we may impose the condition

$$a_0 > 2r_0 \quad (133)$$

where a_0 is the distance between nearest neighbor ions on the lattice. Hence the self-energy of the lattice will not be influenced by the cut-off at r_0 and will still be given by

$$U_0 = v^2 \sum_{\alpha \neq \beta} \sum \frac{1}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} \quad (134)$$

From (132) the following matrix elements $\langle r|v'|s \rangle$ are obtained:

$$\langle r|v'|s \rangle = \delta(\sigma_r, \sigma_s) \sum_{\mathbf{k}} c_{\mathbf{k}} \delta(\mathbf{p}_s - \mathbf{p}_r, \mathbf{k}) \quad (135)$$

with

$$c_{\mathbf{k}} = -\frac{vs}{v_0} \frac{8\pi}{k^2} \cos kr_0 \quad (\mathbf{k} \neq 0) \quad (136)$$

In the particular case $\mathbf{k} = 0$, corresponding to the diagonal elements $\langle r|v'|r \rangle$, we have:

$$c_0 = -\frac{2vs}{v_0} \int_{\Omega} \frac{d\mathbf{r}}{r} + \frac{sv}{v_0} 4\pi r_0^2 \quad (137)$$

From these results it is easy to deduce the modifications introduced in the expression for the ground-state energy by the cut-off in $v'(\mathbf{r})$:

(1) the Madelung term is modified because of the second term of c_0 ; we have:

$$A_{\text{Mad}} = -\bar{N} \left(\frac{\bar{N}}{\Omega} \right)^{\frac{1}{3}} (sv)^{\frac{2}{3}} \chi + 4\pi \left(\frac{\bar{N}^2}{\Omega} \right) r_0^2 \quad (138)$$

(2) the polarization term is obtained at once by replacing the Fourier components $c_{\mathbf{k}}$ in (112) by their value (136):

$$A_{\text{pol}}(\epsilon_F) = -\frac{1}{2} \frac{\bar{N}^2}{\Omega} \epsilon_F^{-\frac{2}{3}} \sum_{\mathbf{u} \neq 0} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \cos^2 \left\{ 2 \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{r_0 u}{r_s} \right\} \quad (139)$$

Finally the ground-state energy per electron is given by:

$$\begin{aligned} \epsilon(r_s) = & \frac{3}{5} \left(\frac{9\pi}{4} \right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{1}{3} \left(\frac{3rs}{\pi} \right)^{\frac{2}{3}} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \chi \frac{1}{r_s} + 3 \frac{r_0^2}{r_s^3} \\ & - \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{1}{r_s} + \{0.0622 \ln r_s - 0.096\} \\ & - \frac{1}{6\pi^2} \sum_{u \neq 0} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \cos^2 \left\{ 2 \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{r_0 u}{r_s} \right\} \end{aligned} \quad (140)$$

On Fig. 8, we plotted the three curves of $\epsilon(r_s)$ corresponding respectively to $r_0 = 1, 1.5$, and 2 . The minimum of these curves moves upward and to the right as r_0 increases.

Another way of looking at this model is to determine the abscissa r_s^* and the ordinate ϵ^* of the minimum in terms of r_0 , and then to plot ϵ^* versus r_s^* on a graph (see Fig. 10). The

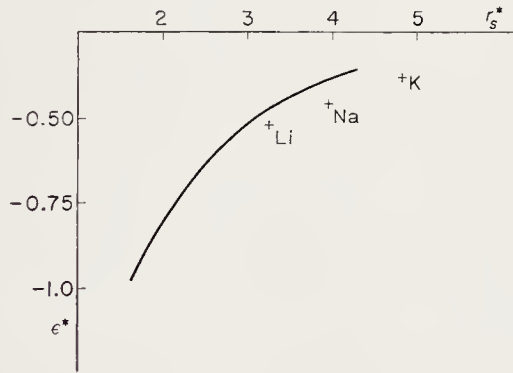


Fig. 10. Plot of ϵ^* versus r_s^* for the modified Coulomb potential. Experimental data for lithium, sodium, and potassium.

experimental points for the first three alkali metals, lithium, sodium, and potassium, fall reasonably close to this curve. It thus seems that quite a large improvement results from the introduction into the model of the cut-off distance r_0 . We must, however, bear in mind that the convergence of the series expansion $\epsilon(r_s)$ becomes questionable for $r_s > 2$. This is why we did

not extend the curve toward larger values of r_s . It is apparent that the slow convergence of the series expansions is the essential limitation to the use of perturbational approaches to the theory of metals.

V. MULTICOMPONENT LATTICES

We now turn to the case of multicomponent lattices. The simplest situation of this type occurs when two types of sites are arranged so as to form a superlattice, since the potential energy of an electron is once again a space-periodic function. We shall also consider the problem of disordered lattices in the random-mixing approximation. More precisely, we shall calculate the ground-state energy for a particular distribution of the positive charges and take the unweighted average of this quantity.

In the same way as in Section IV-E, only the Madelung term and the polarization term are influenced by the replacement of the one-component lattice by a multicomponent one; hence we need only study these contributions in the present section.*

A. Superlattices

This section will be devoted to the calculation of the ground-state energy of an electron gas in a lattice formed by two types of point charges, v_A and v_B , so arranged as to form a superlattice. The various sites of the A lattice will be denoted by $\alpha, \beta, \dots$, while the various sites of the B lattice will be denoted by $i, j, \dots$. The interaction between an electron at $\mathbf{r}$ and the whole lattice is given by the sum:

$$v'(\mathbf{r}) = -v_A \sum_{\alpha} \frac{2}{|\mathbf{r} - \mathbf{R}_{\alpha}|} - v_B \sum_i \frac{2}{|\mathbf{r} - \mathbf{R}_i|} \quad (141)$$

and the self-energy of the lattice may be written as:

$$U_0 = v_A^2 \sum_{\alpha \neq \beta} \frac{1}{|\mathbf{R}_{\alpha} - \mathbf{R}_{\beta}|} + v_B^2 \sum_{i \neq j} \frac{1}{|\mathbf{R}_i - \mathbf{R}_j|} + 2v_A v_B \sum_{\alpha} \sum_i \frac{1}{|\mathbf{R}_{\alpha} - \mathbf{R}_i|} \quad (142)$$

* Part of the results reported in this section are due to Dr. E. Praestgaard. A more detailed account will be given elsewhere.³⁵

In order to simplify the formulae, we shall limit ourselves to equimolar mixtures $A + B$; the superlattice will be formed of the imbrication of two similar lattices A and B of cubic symmetry (simple cubic, body-centered, or face-centered), displaced relative to each other by a certain vector $\mathbf{R}$. As an example, consider a superlattice of body-centered type, such that the corners of the unit cell are occupied by A charges while the center of the cell is occupied by a B charge: then the lattices A and B are simple cubic ones with the same edge a (equal to the edge of the unit cell of the superlattice) and the vector $\mathbf{R}$ is equal to $(a/2, a/2, a/2)$.

From Eqs. (41) and (42) the following matrix elements of v' are obtained:

$$\langle r|v'|s\rangle = \delta(\sigma_r, \sigma_s) \sum_{\mathbf{k}} (c_{\mathbf{k}}^A + c_{\mathbf{k}}^B e^{-i\mathbf{k} \cdot \mathbf{R}}) \delta(\mathbf{p}_r - \mathbf{p}_s, \mathbf{k}) \quad (143)$$

where $\mathbf{k}$ is a vector of the reciprocal lattice of lattice A (or B) and:

$$c_{\mathbf{k}}^A = -\frac{8\pi}{k^2} \frac{s\nu_A}{a^3} \quad c_{\mathbf{k}}^B = -\frac{8\pi}{k^2} \frac{s\nu_B}{a^3} \quad (144)$$

($s = 1, 2, 4$ according to the structure of lattices A and B : simple cubic, body-centered, or face-centered).

With the use of (142) the Madelung contribution to the ground-state energy becomes:

$$\begin{aligned} U_0 - \frac{\bar{N}^2}{2\Omega} \bar{v}(0) &= L(\nu_A^2 + \nu_B^2) \sum_{\alpha \neq 0} \frac{1}{R_\alpha} \\ &+ 2L\nu_A\nu_B \sum_i \frac{1}{|\mathbf{R}_\alpha - \mathbf{R}_i|} - \frac{\bar{N}^2}{\Omega} \int_{\Omega} \frac{1}{r} d\mathbf{r} \end{aligned} \quad (145)$$

where L is the number of sites in each lattice A and B , and advantage has been taken of the fact that the lattices A and B are identical. Due to the condition of electroneutrality:

$$\bar{N}/\Omega = s(\nu_A + \nu_B)/a^3 \quad (146)$$

Eq. (145) becomes:

$$\begin{aligned} U_0 - (\bar{N}^2/2\Omega) \bar{v}(0) &= -(\bar{N}^2/\Omega) a^2 \chi_{A+B} \\ &= -\frac{1}{3} \bar{N} \{3s(\nu_A + \nu_B)/\pi\}^{\frac{2}{3}} (9\pi/4)^{\frac{1}{3}} r_s^{-1} \chi_{A+B} \end{aligned} \quad (147)$$

where χ_{A+B} is given by

$$\begin{aligned}\chi_{A+B} &= \frac{v_A^2 + v_B^2}{(v_A + v_B)^2} \left\{ \int \frac{1}{\tilde{r}} d\tilde{\mathbf{r}} - \frac{1}{s} \sum_{\alpha \neq 0} \frac{1}{\tilde{R}_\alpha} \right\} \\ &\quad + \frac{2v_A v_B}{(v_A + v_B)^2} \left\{ \int \frac{1}{\tilde{r}} d\tilde{\mathbf{r}} - \frac{1}{s} \sum_i \frac{1}{|\tilde{\mathbf{R}}_x - \tilde{\mathbf{R}}_i|} \right\} \\ &= \frac{v_A^2 + v_B^2}{(v_A + v_B)^2} \chi_{AA} + \frac{2v_A v_B}{(v_A + v_B)^2} \chi_{AB}\end{aligned}\quad (148)$$

In this equation $\tilde{r}$ and $\tilde{R}_x$ are dimensionless quantities defined as:

$$\tilde{r} = r/a \quad \tilde{R}_x = R_x/a \quad (149)$$

The constants χ_{AA} and χ_{AB} can be readily calculated for cubic lattices.

The polarization term is obtained by replacing the matrix elements of v' by their values (143) in the corresponding expression (112) for a one-component lattice. Finally, the ground-state energy per electron is given by:

$$\begin{aligned}\epsilon(r_s) &= \frac{3}{5} \left(\frac{9\pi}{4} \right)^{\frac{2}{3}} \frac{1}{r_s^2} - \frac{1}{3} \left\{ \frac{3s(v_A + v_B)}{\pi} \right\}^{\frac{2}{3}} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \chi_{A+B} \frac{1}{r_s} \\ &\quad - \frac{3}{2\pi} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \frac{1}{r_s} + (0.0622 \ln r_s - 0.096) \\ &\quad - \frac{1}{6\pi^2} \sum_{\mathbf{u} \neq 0} \left| \frac{v_A + v_B e^{2\pi i \mathbf{n} \cdot \tilde{\mathbf{R}}}}{v_A + v_B} \right|^2 \frac{1}{u^4} \left\{ \frac{1 - u^2}{2u} \ln \left| \frac{1 + u}{1 - u} \right| + 1 \right\}\end{aligned}\quad (150)$$

where

$$\mathbf{R} = \mathbf{R}/a \quad (151)$$

and

$$\mathbf{u} = \{\pi/3s(v_A + v_B)\}^{\frac{1}{3}} \mathbf{n} \quad (152)$$

n_x, n_y and n_z are integral numbers and one sums over all vectors $\mathbf{u}$ of the reciprocal lattice of lattice A (or B), with the edge of the unit cell equal to $\{\pi/3s(v_A + v_B)\}^{\frac{1}{3}}$.

Let us now apply this general formula to the example given before, i.e., a body-centered cubic lattice of the CsCl type with $v_A = 1$ and $v_B = 2$. As has already been said, the lattices A and B are simple cubic ones ($s = 1$) and

$$\mathbf{R} = (a/2, a/2, a/2) \quad (153)$$

The expression for χ_{A+B} becomes:

$$\chi_{A+B} = \frac{5}{9}\chi_{AA} + \frac{4}{9}\chi_{AB} \quad (154)$$

The value of χ_{AA} is quoted in Table I (simple cubic lattice), while the value of χ_{AB} may be deduced from the values of χ for the simple cubic and the body-centered cubic lattices; indeed one may readily verify that the following relation must hold:

$$\chi_{b.c.c.} = \frac{1}{2}(\chi_{s.c.} + \chi_{AB}) \quad (155)$$

Using Table I we find:

$$\chi_{AB} = 0.8019 \quad (156)$$

and

$$\chi_{A+B} = 1.9327 \quad (157)$$

On the other hand, the polarization term takes here the following form:

$$-\frac{1}{6\pi^2} \sum_{\mathbf{u} \neq 0} \frac{|1 + 2(-)^{n_x+n_y+n_z}|^2}{9} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \quad (158)$$

where:

$$\mathbf{u} = (\pi/9)^{\frac{1}{3}} \mathbf{n}$$

i.e., $\mathbf{u}$ is any vector of a simple cubic lattice with an edge $(\pi/9)^{\frac{1}{3}}$; (158) may still be written as

$$-\frac{1}{6\pi^2} \left\{ \sum_{\mathbf{u}_1 \neq 0} + \frac{1}{9} \sum_{\mathbf{u}_2} \right\} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \quad (159)$$

In this expression, the vectors $\mathbf{u}_1$ form a face-centered cubic lattice with an edge $2(\pi/9)^{\frac{1}{3}}$, and the vectors $\mathbf{u}_2$ form a lattice of

the same type, but displaced with respect to the first one by a vector $2(\pi/9)^{\frac{1}{2}}\{\frac{1}{2}, 0, 0\}$. Both sums have been calculated numerically:

$$\sum_{\mathbf{u}_1 \neq 0} = 14.33 \quad (160)$$

and

$$\sum_{\mathbf{u}_2} = 43.41$$

Using (157) and (160), one can draw a curve for $\epsilon(r_s)$ in terms of r_s which is quite similar to the one given in Fig. 8 for a one-component lattice. We shall merely give the values of the abscissa and ordinate of the minimum of this curve:

$$\epsilon^{\star} = -1.720 \quad r_s^{\star} = 1.27 \quad (161)$$

In order to see if our superlattice model could be an adequate representation of a binary alloy, we now have to compare the value of $\epsilon^{\star}$ calculated above with the corresponding values for the "pure" phases A and B. Let us imagine that the "metals" A and B form simple cubic lattices. We then know from Section IV that the minimum energy for metal A ($\nu_A = 1$) is equal to $\epsilon_A^{\star} = -0.992$. In the same way, we find for metal B ($\nu_B = 2$) the value $\epsilon_B^{\star} = -2.117$. The energy of mixing for metals A and B to form an A-B superlattice is then given by:

$$\epsilon_M = \frac{3}{2}\epsilon^{\star} - \frac{1}{2}\epsilon_A^{\star} - \epsilon_B^{\star} \quad (162)$$

$$= +0.033 \text{ Ry} \quad (163)$$

Hence the mixture is found to be unstable. General conclusions cannot, of course, be drawn from this single result. Indeed, the energy of mixing might well be very sensitive to the lattice structure, although this is not the case for the one-component lattices. In fact, more detailed calculations are now being carried out in which different lattice structures as well as different charges ν_A and ν_B are considered.*

* While the present article was in press, the above calculations were generalized to take account of the structure of the ions. The results will be published soon.³⁷

B. Disordered Lattice

To approach the problem of a disordered lattice, we shall proceed in the following way. Let us consider a lattice on the sites of which are distributed L_A point charges ν_A and L_B point charges ν_B , with

$$L_A + L_B = L \quad (164)$$

the total number of sites. The mole fractions of A and B in the mixture are given by:

$$x_A = L_A/L \quad x_B = L_B/L \quad (165)$$

Let us now separate the charge ν_α of any site α into two parts by writing:

$$\nu_\alpha = \langle \nu \rangle + \nu'_\alpha \quad (166)$$

where $\langle \nu \rangle$ is the average value of ν_α , i.e.,

$$\langle \nu \rangle = x_A \nu_A + x_B \nu_B \quad (167)$$

This procedure, of course, induces a similar separation for the potential $v'(\mathbf{r})$ as given by (35):

$$v'(\mathbf{r}) = -2\langle \nu \rangle \sum_{\alpha} \frac{1}{|\mathbf{r} - \mathbf{R}_{\alpha}|} - 2 \sum_{\alpha} \frac{\nu'_\alpha}{|\mathbf{r} - \mathbf{R}_{\alpha}|} \quad (168)$$

We shall calculate the ground-state energy of an electron gas, in a lattice of the type just described, for any particular distribution of the charges ν_A and ν_B over the sites α , and then take the average of this result over all distributions. We consider that the charges are located at random. If we limit ourselves to terms of second order in the interaction strength, we shall only need averages of the two following types: $\langle \nu'_\alpha \rangle$ and $\langle \nu'_\alpha \nu'_\beta \rangle$. In the random-mixing approximation, taking account of (165), we get:

$$\langle \nu'_\alpha \rangle = 0 \quad (169)$$

$$\langle \nu'_\alpha \nu'_\beta \rangle = O(1/L) \quad \text{for } \alpha \neq \beta \quad (170)$$

and

$$\begin{aligned} \langle \nu'^2_\alpha \rangle &= x_A \nu'^2_A + x_B \nu'^2_B \\ &= x_A x_B (\nu_A - \nu_B)^2 \end{aligned} \quad (171)$$

Let us first calculate the Madelung term. Substituting (166) into the definition (34) of the lattice self-energy, we get:

$$U_0 - \frac{\bar{N}^2}{2\Omega} \bar{v}(0) = \sum_{\alpha \neq \beta} \sum \frac{(\langle v \rangle + v'_\alpha)(\langle v \rangle + v'_\beta)}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} - \frac{\bar{N}^2}{\Omega} \int \frac{1}{r} d\mathbf{r} \quad (172)$$

Now we have to take the average of this expression. Taking account of (169)–(171) and neglecting terms of order $O(1/N)$, we see at once that the charges v'_α will play no role in the averaged Madelung energy, which is simply given by:

$$\langle v \rangle^2 \sum_{\alpha \neq \beta} \sum \frac{1}{|\mathbf{R}_\alpha - \mathbf{R}_\beta|} - \frac{\bar{N}^2}{\Omega} \int \frac{1}{r} d\mathbf{r} \quad (173)$$

Using the condition for electrical neutrality, which may here be written in the following form:

$$\bar{N}/\Omega = s\langle v \rangle/a^3 \quad (174)$$

we finally arrive at:

$$\begin{aligned} U_0 - \frac{\bar{N}^2}{2\Omega} \bar{v}(0) &= -\frac{\bar{N}^2 a^2}{\Omega} \chi \\ &= -\frac{\bar{N}}{3} \left(\frac{3s\langle v \rangle}{\pi} \right)^{\frac{2}{3}} \left(\frac{9\pi}{4} \right)^{\frac{1}{3}} \chi \frac{1}{r_s} \end{aligned} \quad (175)$$

where χ is the same constant as defined by (99) for the case of a one-component lattice. Thus the Madelung contribution to the ground-state energy of the system is the same as that due to a one-component lattice of point charges $\langle v \rangle$.

Let us now proceed to the evaluation of the polarization term. We must first calculate the matrix elements of the potential $v'(\mathbf{r})$ as given in (168); going back to (42), we see that $\bar{v}'(\mathbf{p})$ will separate into two parts:

$$\bar{v}'(\mathbf{p}) = -\frac{8\pi}{p^2} \langle v \rangle \sum_{\alpha} e^{i\mathbf{p} \cdot \mathbf{R}_\alpha} - \frac{8\pi}{p^2} \sum_{\alpha} v'_\alpha e^{i\mathbf{p} \cdot \mathbf{R}_\alpha} \quad (176)$$

Using Eq. (91) we get :

$$\langle r|v'|s\rangle = \delta(\sigma_r, \sigma_s) \left\{ \sum_{\mathbf{k}} c_{\mathbf{k}} \delta(\mathbf{p}_r - \mathbf{p}_s, \mathbf{k}) - \frac{1}{\Omega} \frac{8\pi}{|\mathbf{p}_r - \mathbf{p}_s|^2} \sum_{\alpha} v'_{\alpha} e^{i(\mathbf{p}_r - \mathbf{p}_s) \cdot \mathbf{R}_{\alpha}} \right\} \quad (177)$$

where

$$c_{\mathbf{k}} = - \frac{8\pi}{k^2} \frac{s\langle v \rangle}{a^3} \quad (178)$$

$\mathbf{k}$ being a vector of the reciprocal lattice. Thus, we observe that the matrix elements $\langle r|v'|s\rangle$ consist of two essentially different parts: the first, due to the average charge $\langle v \rangle$, has, of course, the same structure as that found for a one-component lattice and only differs from zero when $\mathbf{p}_r - \mathbf{p}_s$ is equal to a vector of the reciprocal lattice. The second term, which takes care of the fluctuation of the charge v_{α} , exists for all $\mathbf{p}_r - \mathbf{p}_s$, and we shall ultimately need to integrate it over this continuous variable (at the limit $\Omega \rightarrow \infty$).

When we evaluate the contribution of the last diagram of Fig. 1d, which is given by

$$- \sum_{\mathbf{p}_r \neq \mathbf{p}_s} \sum_{\sigma_r \sigma_s} |\langle r|v'|s\rangle|^2 \frac{1}{p_r^2 - p_s^2} f_r^+ f_s^- \quad (179)$$

the two terms in $\langle r|v'|s\rangle$ lead to four terms:

(a) The first term contains two interactions with the Fourier component $c_{\mathbf{k}}$ of the "average charge potential" and is clearly identical with the contribution calculated for a one-component lattice of charges $\langle v \rangle$; per electron we find:

$$- \frac{1}{6\pi^2} \sum_{\mathbf{u} \neq 0} \frac{1}{u^4} \left\{ \frac{1 - u^2}{2u} \ln \left| \frac{1 + u}{1 - u} \right| + 1 \right\}$$

where

$$\mathbf{u} = (\pi/3s\langle v \rangle)^{\frac{1}{3}} \mathbf{n}$$

(b) In the second and third terms, there will be one interaction with the average charge $\langle v \rangle$ and one with the fluctuating charge v' . From (176) these contributions will be proportional to

$$\sum_{\alpha} v'_{\alpha} e^{i\mathbf{p} \cdot \mathbf{R}_{\alpha}}$$

i.e., linear in ν'_α , and when we average them over all random distributions of the ions, it follows at once from (169) that these terms vanish.

(c) In the fourth term, there will be two interactions with the fluctuating charge ν'_α . Substituting the second part of (176) into (179), we get:

$$-\sum_{\sigma} \sum_{\mathbf{p} \neq \mathbf{p}'} \frac{1}{\Omega^2} \left(\frac{8\pi}{|\mathbf{p}' - \mathbf{p}|^2} \right)^2 \frac{1}{p'^2 - p^2} f_{\mathbf{p}'}^+ f_{\mathbf{p}}^- \sum_{\alpha} \sum_{\beta} \nu'_\alpha \nu'_\beta e^{i(\mathbf{p}' - \mathbf{p}) \cdot (\mathbf{R}_\alpha - \mathbf{R}_\beta)} \quad (180)$$

Averaging this expression over the distributions of the positive charges on the lattice sites and taking account of Eqs. (170) and (171), we see that only the contributions where $\alpha = \beta$ will be significant. Hence, summing over the two spin possibilities, taking the limits $\Omega \rightarrow \infty$ and $\beta \rightarrow \infty$ and introducing a new variable $\mathbf{q}$:

$$\mathbf{p}' = \mathbf{p} + \mathbf{q} \quad (181)$$

we arrive at:

$$-\frac{2L\langle \nu'^2 \rangle}{\pi^4} \int d\mathbf{q} \frac{1}{q^4} \int_{\substack{p > P \\ |\mathbf{p} + \mathbf{q}| > P}} d\mathbf{p} \frac{1}{|\mathbf{p} + \mathbf{q}|^2 - p^2} \quad (182)$$

Using reduced variables

$$\tilde{\mathbf{q}} = \mathbf{q}/P \quad \tilde{\mathbf{p}} = \mathbf{p}/P$$

Eq. (182) transforms into:

$$-\frac{L\langle \nu'^2 \rangle}{\pi^4} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^4} \int_{\substack{\tilde{p} < 1 \\ |\tilde{\mathbf{p}} + \tilde{\mathbf{q}}| > 1}} d\tilde{\mathbf{p}} \frac{1}{\tilde{\mathbf{p}} \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \quad (182')$$

We have:

$$\Phi(\tilde{q}) = \int_{\substack{\tilde{p} < 1 \\ |\tilde{\mathbf{p}} + \tilde{\mathbf{q}}| > 1}} d\tilde{\mathbf{p}} \frac{1}{\tilde{\mathbf{p}} \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} = \pi \left\{ \left(\frac{2}{\tilde{q}} - \frac{\tilde{q}}{2} \right) \frac{1}{2} \ln \left| \frac{1 + \tilde{q}/2}{1 - \tilde{q}/2} \right| + 1 \right\} \quad (183)$$

and for $\tilde{q}$ small,

$$\Phi(\tilde{q}) = 2\pi - \frac{\pi}{6} \tilde{q}^2 - \frac{\pi}{120} \tilde{q}^4 + O(\tilde{q}^6) \quad (184)$$

i.e., $\Phi(\tilde{q}) \rightarrow 2\pi$ for $\tilde{q} \rightarrow 0$. Hence, the integral over $\tilde{\mathbf{q}}$ in (182') diverges. We know (see Section III-A) that to get rid of divergences of this type, we have to look for a family of diagrams which diverge in the same way and sum their contributions before integrating over $\tilde{\mathbf{q}}$. A few of these diagrams are shown in Fig. 11.

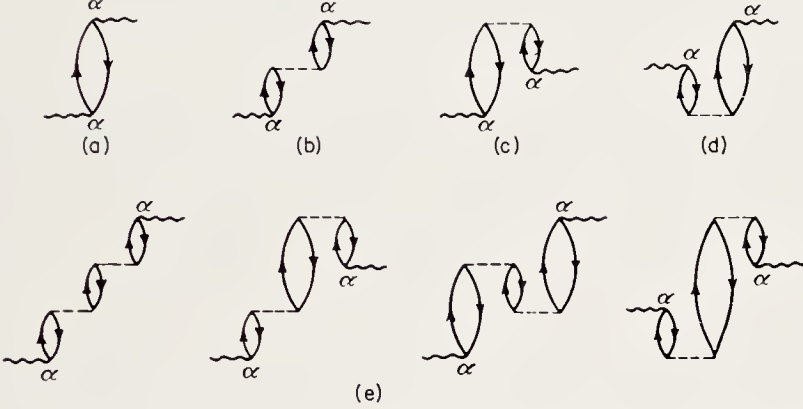


Fig. 11. Diagrams contributing to the fluctuating charge polarization term. (a) Second-order diagram; (b)–(d) third-order diagrams; (e) a few of the twelve fourth-order diagrams.

Let us write down the contributions of the three third-order diagrams (b), (c), and (d). They only differ through their energy denominators; adding them together, we obtain:

$$\begin{aligned}
 \frac{L\langle v_x'^2 \rangle}{\pi^6} \frac{1}{P} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^6} \int_{\substack{\tilde{p}_1 < 1 \\ |\tilde{\mathbf{p}}_1 + \tilde{\mathbf{q}}| > 1}}^{\substack{\tilde{p}_2 < 1 \\ |\tilde{\mathbf{p}}_2 + \tilde{\mathbf{q}}| > 1}} d\tilde{\mathbf{p}}_1 d\tilde{\mathbf{p}}_2 \left\{ \frac{1}{\tilde{\mathbf{p}}_1 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \frac{1}{\tilde{\mathbf{p}}_2 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \right. \\
 + \frac{1}{\tilde{\mathbf{p}}_1 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \frac{1}{\tilde{\mathbf{p}}_1 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2 + \tilde{\mathbf{p}}_2 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \\
 \left. + \frac{1}{\tilde{\mathbf{p}}_1 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2 + \tilde{\mathbf{p}}_2 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \frac{1}{\tilde{\mathbf{p}}_2 \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2} \right\} \quad (185)
 \end{aligned}$$

Now if we define:

$$a_i = \tilde{\mathbf{p}}_i \cdot \tilde{\mathbf{q}} + \frac{1}{2}\tilde{q}^2 \quad (186)$$

we see that the sum between the brackets may be written as:

$$\frac{1}{a_1 a_2} + \frac{1}{a_1(a_1 + a_2)} + \frac{1}{(a_1 + a_2)a_2} = \frac{2}{a_1 a_2} \quad (187)$$

whence the integrals over $\tilde{\mathbf{p}}_1$ and $\tilde{\mathbf{p}}_2$ in (185) factorize into a product of integrals such as (183) and we get:

$$\frac{L\langle v_\alpha'^2 \rangle}{\pi^6} \frac{1}{P} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^6} 2[\Phi(\tilde{q})]^2 \quad (188)$$

The reader will readily convince himself that a relation like (187) holds at all orders, i.e., that the sum of the energy denominators appearing in all contributions at order n is equal to

$$2^{n-2} / \prod_{i=1}^{n-1} a_i \quad (189)$$

Hence the general expression for the n th order contribution to the family of diagrams we are considering takes the form

$$\frac{L\langle v_\alpha'^2 \rangle P}{2\pi^2} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^2} \left(\frac{-2\Phi(\tilde{q})}{P\pi^2 \tilde{q}^2} \right)^{n-1} \quad (190)$$

We now have to sum this expression over n from two to infinity and integrate the result over $\tilde{\mathbf{q}}$. But, in fact, we do not want to retain contributions of order higher than the second in the strength of the interaction λ . Therefore, for $n > 2$ in (190), we must only retain the part of $\Phi(\tilde{q})$ which leads to the strongest divergence of the integral for $\tilde{q}$ small, i.e., the constant term 2π in the power series (184). Let us then separate $\Phi(\tilde{q})$ into two parts by defining

$$\Phi(\tilde{q}) = 2\pi + \Phi'(\tilde{q}) \quad (191)$$

The second-order contribution (182) yields two terms:

$$-\frac{L\langle v_\alpha'^2 \rangle}{\pi^4} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^4} 2\pi \quad (192)$$

which diverges for $\tilde{q} \rightarrow 0$, and

$$-\frac{L\langle v_\alpha'^2 \rangle}{\pi^4} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^4} \Phi'(\tilde{q}) \quad (193)$$

which is finite. In all other terms $n > 2$, we may neglect $\Phi'(\tilde{q})$. Consequently, in the sum over n of expression (190), we need to take

- (1) the finite second-order term (193);
- (2) the series

$$\frac{L\langle v_\alpha'^2 \rangle P}{2\pi^2} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^2} \sum_{n=1}^{\infty} \left(\frac{-4\pi}{P\pi^2 \tilde{q}^2} \right)^n = -\frac{2L\langle v_\alpha'^2 \rangle}{\pi^3} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^2} \frac{1}{\tilde{q}^2 + 4/\pi P} \quad (194)$$

which is readily seen to be finite. For (193), we find after integration:

$$-\frac{L\langle v_\alpha'^2 \rangle}{\pi^3} \int d\tilde{\mathbf{q}} \frac{1}{\tilde{q}^4} \left\{ \left(\frac{2}{\tilde{q}} - \frac{\tilde{q}}{2} \right) \frac{1}{2} \ln \left| \frac{1 + \tilde{q}/2}{1 - \tilde{q}/2} \right| - 1 \right\} = \frac{L\langle v_\alpha'^2 \rangle}{2} \quad (195)$$

while (194) leads to

$$- [2L\langle v_\alpha'^2 \rangle / \pi^{\frac{1}{2}}] P^{\frac{1}{2}} \quad (196)$$

which is of order $O(3/2)$ in the interaction strength (i.e., $\sim e^3$).

We have thus shown that, besides [the Madelung and the polarization terms corresponding to a lattice of average charges $\langle v \rangle$], the contribution of the electron-lattice interactions to the ground-state energy of an electron gas in a randomly disordered lattice contains two additional terms of order $O(3/2)$ and $O(2)$, proportional to the fluctuation $\langle v_\alpha'^2 \rangle$ of the charge on any site α . Indeed, taking into account (174), (175), (195), and (196), we arrive at the following expression for the ground-state energy per electron:

$$\begin{aligned} \epsilon(r_s) &= \epsilon^0(r_s, \langle v \rangle) - \frac{\langle v_\alpha'^2 \rangle}{\langle v \rangle} \left\{ \frac{2}{\pi^{\frac{1}{2}}} \left(\frac{9\pi}{4} \right)^{\frac{1}{2}} \frac{1}{r_s^{\frac{1}{2}}} - \frac{1}{2} \right\} \\ &= \epsilon^0(r_s, \langle v \rangle) - x_A x_B \frac{(v_A - v_B)^2}{x_A v_A + x_B v_B} \left\{ \frac{2}{\pi^{\frac{1}{2}}} \left(\frac{9\pi}{4} \right)^{\frac{1}{2}} \frac{1}{r_s^{\frac{1}{2}}} - \frac{1}{2} \right\} \quad (197) \end{aligned}$$

where $\epsilon^0(r_s, \langle v \rangle)$ represents the ground-state energy of the system for a one-component lattice of point charges $\langle v \rangle$, as given by (130).

As an example, let us now apply this general formula to the particular case of a 50% mixture of charges $v_A = 1$ and $v_B = 2$

distributed at random over a body-centered cubic lattice. This system corresponds to the example considered in the preceding section, where the charges v_A and v_B were fixed at definite positions so as to form a superlattice.

We have here:

$$x_A = x_B = 0.5 \quad (198)$$

and

$$\langle v \rangle = 1.5 \quad |v_A - v_B| = 1 \quad (199)$$

The polarization term appearing in $\epsilon^0(r_s, \langle v \rangle)$ is of the usual form:

$$-\frac{1}{6\pi^2} \sum_{\mathbf{u} \neq 0} \frac{1}{u^4} \left\{ \frac{1-u^2}{2u} \ln \left| \frac{1+u}{1-u} \right| + 1 \right\} \quad (200)$$

with

$$\mathbf{u} = (\pi/9)^{\frac{1}{3}} \mathbf{n} \quad (201)$$

the vectors $\mathbf{n}$ forming a face-centered cubic lattice with lattice distance equal to 2. The value of this sum is:

$$\sum_{\mathbf{u} \neq 0} = 14.33 \quad (202)$$

We may once again draw a curve for $\epsilon(r_s)$ in terms of r_s . The minimum of this curve is located at:

$$\epsilon^* = -1.67_5 \quad r_s^* = 1.24 \quad (203)$$

With the help of the values of ϵ^* given in Section V-A for the "pure metals" A and B, we may calculate the energy of mixing per lattice site:

$$\epsilon_M = \frac{3}{2}\epsilon^* - \frac{1}{2}\epsilon_A^* - \epsilon_B^* = 0.100 \text{ Ry} \quad (204)$$

Hence the random mixture is found to be more unstable than the superlattice structure considered in Section V-A. Of course, here again one cannot draw general conclusions from this single example and many more numerical computations are necessary.*

VI. CONCLUSIONS

It is not yet possible to draw definite conclusions concerning this kind of approach to the theory of metals; many more numerical computations will be necessary and eventually contributions of order λ^3 should also be retained in the ground-state energy.

* See the footnote on page 134.

One thing that is clear, however, is that the crudest model of positive point charges is definitely inadequate for actual metals. The modified Coulomb potential, however, gives some hope of being able to represent the real situation roughly; thus, a given metal in this picture should be characterized by two parameters:

- (i) the ionic charge ν (i.e., the number of "free electrons") and
- (ii) the radius of the ion core r_0 .

If valid, such a crude theory of metals should in a certain sense be analogous to the cell theory of ordinary liquids, which also involves two molecular parameters ϵ and σ .³⁶ It would then be possible to develop along the same lines a theory of metallic solutions. The excess thermodynamic properties of a mixture of two metals A and B would then depend on the differences $(\nu_A - \nu_B)$ and $(r_{0A} - r_{0B})$. That this theory is very rough for pure metals is not a limitation for its applicability to mixtures; it is indeed well known from the theory of non-electrolyte solutions that the properties of mixtures may be reasonably analyzed from rather crude statistical models.

The authors are much indebted to Professor Prigogine for constant help and advice during this work; they also want to thank Drs. Fujita, Heine, and Cohen for stimulating discussions.

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ON THE THERMODYNAMICS OF SURFACE SYSTEMS

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I. INTRODUCTION

The fact that a consistent thermodynamic theory which in detail can account for both adsorption and surface tension at planar surfaces has not yet been established has been regarded by many physical chemists as rather unsatisfactory. The theory of capillary formulated by Gibbs¹ gives, owing to the use of excess functions, general relations of a limited practical value. Different readers have drawn controversial conclusions when studying

Gibbs' text. This is especially true of the question as to what value should be given to the chemical potential μ_i of a substance when it is placed in a surface phase. Whilst Butler² has shown that for a monolayer an equilibrium condition implying that $\mu_i^s \neq \mu_i^b$ (s denotes a surface phase and b a bulk phase) is consistent with Gibbs' theory, Guggenheim³ states without further argument that μ_i must have the same value throughout a system when physico-chemical equilibrium prevails, and his treatment is obviously a modification of Gibbs'. Gibbs' own derivation of his adsorption law does not contain much reasoning concerning the method he chose for treating surface effects. Because of this some writers have felt doubts about its validity. Recently, de Witte⁴ has challenged various proofs of Gibbs' law and has, like Kofoed and Villadsen,⁵ pointed out that there should be an analogy between electrochemical potentials and surface-chemical potentials.

The following treatment should be regarded as an attempt to obtain a straightforward application of the thermodynamic theory to systems containing planar surface phases with the aim of scrutinizing the difficulties mentioned. The interest will mainly be focused on problems related to the equilibrium properties at constant T and p , thus excluding the explicit study of changes due to temperature and pressure variations.

II. PHYSICAL CONSIDERATIONS

Consider a *closed system in equilibrium* consisting of k constituents which may be dependent, implying that some constituents can be formed out of others. The system is assumed to contain two homogeneous bulk phases, b' and b'' , separated by a common planar surface phase, s . Each of the phases is supposed to contain all the constituents. We are primarily interested in liquid-gas and liquid-liquid systems for which the interfacial area can be varied at will, the system always remaining a two-bulk-phase system. Suppose that there are no charged species present. If magnetic and gravitational energies are neglected, the energy content of the system can be increased in three ways only, namely by supply of heat, pV -work and surface work. Generally, as was stated by Gibbs,⁶ it is reasonable to assume that

extraordinary conditions prevail in the vicinity of the interface, especially with regard to such properties as energy, entropy, and composition per unit volume. The nonuniform surface region, called the surface phase, cannot be treated as an ordinary phase just because it is not homogeneous in these properties. There must, for example, always be a more or less gradual change in the composition in a surface phase. The exact positions of the boundaries between the surface phase and the bulk phases are thus difficult to prescribe *a priori*. Nevertheless, the concept of a *physical* surface phase is conceivable, implying that only the region with properties appreciably differing from the bulk phase properties is included. The subsequent treatment primarily relies upon considerations of the physical surface phase.

Because the surface phase in question is built up of the substances present in the bulk phases, it is necessary to associate an increase of the interfacial area with a *transport reaction* of the character (where ' and '' refer to the bulk phases and B denotes the chemical symbol)

$$\begin{aligned}
 & \nu_1^{t'} B'_1 + \nu_2^{t'} B'_2 + \dots + \nu_i^{t'} B'_i + \dots + \nu_k^{t'} B'_k \\
 & + \nu_1^{t''} B''_1 + \nu_2^{t''} B''_2 + \dots + \nu_i^{t''} B''_i + \dots + \nu_k^{t''} B''_k \\
 & = \nu_1^t B_1^b + \nu_2^t B_2^b + \dots + \nu_i^t B_i^b + \dots + \nu_k^t B_k^b \\
 & \rightarrow \nu_1^t B_1^s + \nu_2^t B_2^s + \dots + \nu_i^t B_i^s + \dots + \nu_k^t B_k^s
 \end{aligned} \tag{1a, b}$$

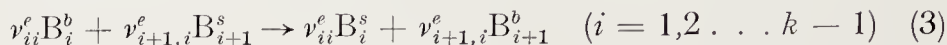
since, at least under conditions of constant temperature and pressure, there is no means of increasing the area at a fixed material content of the physical surface phase, which, on account of its nature, is always inseparably connected to the adjacent bulk phases. When the increase of area is carried out reversibly, reaction (1) proceeds under equilibrium conditions. The stoichiometric coefficients $\nu_i^t = \nu_i^{t'} + \nu_i^{t''}$ then indicate the equilibrium composition of the surface phase provided that equilibrium with respect to the $2(k-1)$ independent *exchange reactions*

$$\nu_{ii}^{e'} B'_i + \nu_{i+1,i}^{e'} B_{i+1}^s \rightarrow \nu_{ii}^{e''} B_i^s + \nu_{i+1,i}^{e''} B'_{i+1} \tag{2a}$$

($i = 1, 2, \dots, k-1$)

$$\nu_{ii}^{e''} B''_i + \nu_{i+1,i}^{e''} B_{i+1}^s \rightarrow \nu_{ii}^{e'''} B_i^s + \nu_{i+1,i}^{e'''} B''_{i+1} \tag{2b}$$

which occur at *constant surface area* is always established. These reactions are described in a less detailed manner by



where the stoichiometric coefficient ν_{ii}^e equals the sum $\nu_{ii}^{e'} + \nu_{ii}^{e''}$, etc. By linear combination of the above exchange reactions, an exchange reaction between any two constituents can, as is easily verified, be obtained.

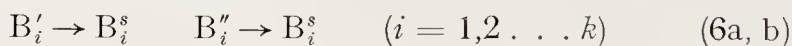
Since the system is in equilibrium, the affinity for the k *transfer reactions* between the two bulk phases



is zero. It appears from Eqs. (2) and (4) that the total number of independent exchange and transfer reactions equals $2k - 1$, since the reactions (2b) may be deduced by combining (2a) and (4) taking into account the reasonable assumption that

$$\nu_{i+1,i}^{e'}/\nu_{ii}^{e'} = \nu_{i+1,i}^{e''}/\nu_{ii}^{e''} \quad (i = 1, 2 \dots k-1) \quad (5)$$

Thus, the reactions (2a) and (4) give a complete description. It may also be deduced upon combining (1), (2a), and (4) that a description using the transport reaction and the exchange and transfer reactions is equivalent to a description based on the $2k$ *molecular transport* reactions



In some connections a distinction between B_i' and B_i'' is not required and it is then sufficient to consider only the k molecular transport reactions



which may be derived by combining Eqs. (1b) and (3).

When the constituents are interdependent, r independent chemical equilibrium reactions

$$\sum_i \nu_{i,p}^c B_i^b = 0 \quad (p = 1, 2 \dots r) \quad (8)$$

occur. Some of these reactions occur in the b' -phase and the others in the b'' -phase. It is obvious that the above reactions give a complete description since the corresponding surface

reactions and reactions in the other bulk phase may be derived from (8) and (6).

Because the system considered is in equilibrium and has a planar surface, it is necessary to assume that the temperature and the pressure are the same throughout the system, otherwise irreversible flows of heat and matter would occur.

We now put forward the idea that an adsorption reaction should generally be regarded as an exchange reaction and *not* as a molecular transport reaction and that a transport reaction cannot occur unless the magnitude of the surface area is varied or, which is an equivalent statement, the area A and the extent ξ^t of the transport reaction (1) are dependent variables, i.e., that there is a relation $A = \text{const.} \times \xi^t$. The character and consequences of these suppositions shall be investigated in the subsequent treatment.

III. THE ENERGY DIFFERENTIAL FOR AN EQUILIBRIUM SURFACE SYSTEM

When deriving a differential expression for the energy it is, as is well known, only necessary to consider *quasi-static* energy increments, which must, however, be independent. According to the first law we have

$$dU = \mathbf{d}q + \mathbf{d}w \quad (9)$$

where q indicates heat and w work. The differential sign d denotes a complete differential and $\mathbf{d}$ a differential that depends upon the way it is chosen to achieve a given change of state. The quasi-static work for the considered system is

$$\mathbf{d}w = -p \, dV + \gamma \, dA \quad (10)$$

and the quasi-static heat is given by the second law simply as

$$\mathbf{d}q = T \, dS \quad (11)$$

because $\mathbf{d}_i S = \mathbf{d}q'/T = 0$, q' denoting the Clausius non-compensated heat. Thus, the energy differential for an equilibrium surface system is

$$dU = T \, dS - p \, dV + \gamma \, dA \quad (12)$$

We now enquire whether it is possible to account for the energy differential using other variables. From the definition of the chemical potential given by Gibbs, strictly valid only for homogeneous masses, it follows that the energy required at constant entropy and volume to bring a differential amount of a substance reversibly from a region where the chemical potential is μ_i^1 to a region where it is μ_i^2 equals $(\mu_i^2 - \mu_i^1) dn_i$. A reversible increase of the interfacial area appears from Eq. (1) to be associated with a reversible transport of molecules to the surface phase. Thus a physically equivalent energy differential expression might be obtained if we put

$$\gamma dA = \sum_i v_i^t (\mu_i^s - \mu_i^b) d\xi^t \quad (13)$$

where use has been made of the fact that the equilibrium condition for the transfer reactions (4) is

$$\mu_i' = \mu_i'' = \mu_i^b \quad (i = 1, 2 \dots k) \quad (14)$$

(The way of reasoning we have used here comprises, according to the energetics of Brönsted,⁷ a *coupling* of two *basic* processes, viz., the mechanical process of increasing the interfacial area and the transport of substances to the surface phase. A quasi-static process is always made up of coupled basic processes.)

However, as equilibrium is also established with respect to the exchange reactions we may add to the right-hand side of (13) the following equilibrium conditions for the reactions (3) (A_i^e denoting the affinity for the i th exchange reaction and $\delta\xi_i^e$ the corresponding *virtual* variation of the reaction coordinate)

$$-A_i^e \delta\xi_i^e = [v_{ii}^e (\mu_i^s - \mu_i^b) - v_{i+1,i}^e (\mu_{i+1}^s - \mu_{i+1}^b)] \delta\xi_i^e = 0 \quad (15) \\ (i = 1, 2 \dots k - 1)$$

without affecting the validity of the equality in question. Since the transport reaction (1b) and the exchange reactions (3) are together equivalent to the k molecular transport reactions (7) we may thus write

$$\gamma \delta A = \sum (\mu_i^s - \mu_i^b) \delta\xi_i^m \quad (16)$$

where ξ_i^m denotes the extent of a molecular transport reaction. But, as is easily established,

$$\delta n_i^s = \delta \xi_i^m \quad (17)$$

and

$$\delta n_i^b = -\delta \xi_i^m + \sum_p \nu_{i,p}^c \delta \xi_p^c \quad (18)$$

From these equations it follows that

$$\sum_i \mu_i^b \delta n_i^b = -\sum_i \mu_i^b \delta n_i^s \quad (19)$$

because the equilibrium condition for the chemical reactions (8) is

$$-A_p^e = \sum_i \nu_{i,p}^c \mu_i^b = 0 \quad p = (1, 2 \dots r) \quad (20)$$

Consequently, it may be stated that

$$\gamma \delta A = \sum_i (\mu_i^s - \mu_i^b) \delta n_i^s \quad (21)$$

where, of course, all n_i^s should be regarded as independent variables, and it is found that the energy differential in the case of internal equilibrium may also be written

$$\delta U = T \delta S - p \delta V + \sum_i \mu_i^s \delta n_i^s + \sum_i \mu_i^b \delta n_i^b \quad (22)$$

The above equations need some comment. In the first place the surface phase may presumably not be regarded as a homogeneous phase and consequently the chemical potential μ_i^s is not strictly defined. n_i^s is also not sharply defined because the boundaries of the surface phase cannot be prescribed. However, as will be shown subsequently, more precise definitions of these quantities can be given.

IV. GIBBS' ADSORPTION LAW

We shall next show how the Gibbs' fundamental equation for a surface phase may be obtained from the above approach. Since U , S , and V are additive properties, it is possible to write

$$\delta U = \delta U^s + \delta U^b, \text{ etc.} \quad (23)$$

and Eq. (22) splits into two equations

$$\delta U^b = T \delta S^b - p \delta V^b + \sum_i \mu_i^b \delta n_i^b \quad (24)$$

$$\delta U^s = T \delta S^s - p \delta V^s + \sum_i \mu_i^s \delta n_i^s \quad (25)$$

because it is required for equilibrium that

$$T = T^b = T^s \quad p = p^b = p^s \quad (26a, b)$$

Now using Eq. (21), Eq. (25), which refers to the physical surface phase, may be written

$$\delta U^s = T \delta S^s - p \delta V^s + \sum_i \mu_i^b \delta n_i^s + \gamma \delta A \quad (27)$$

From an entirely different starting-point, Gibbs deduced the same equation for a planar surface layer also containing parts of the adjacent bulk phases.⁸ But either of the Eqs. (25) and (27) can be integrated, corresponding physically to a building-up of the systems' surface area at constant T , p and composition. On comparing the relations obtained with Eqs. (25) and (27) it is found that

$$0 = S^s \delta T - V^s \delta p + \sum_i n_i^s \delta \mu_i^s \quad (28a)$$

$$- A \delta \gamma = S^s \delta T - V^s \delta p + \sum_i n_i^s \delta \mu_i^b \quad (28b)$$

These two relationships are analogous to the Gibbs-Duhem equation for a homogeneous phase according to which

$$0 = S^{(')} \delta T - V^{(')} \delta p + \sum_i n_i^{(')} \delta \mu_i^b \quad (29a)$$

$$0 = S^{(')} \delta T - V^{(')} \delta p + \sum_i n_i^{(')} \delta \mu_i^b \quad (29b)$$

where (') and (") refer to two parts of the bulk phases b' and b'' . Consequently, only k of the variables T , p , μ_1^b , μ_2^b . . . in Eq. (28b) may be regarded as independent assuming a system with independent components [i.e. no reactions (8)] is treated. The Gibbs excess functions are now conveniently introduced by

$$\begin{aligned} U^E &= U^s - U^{(')} - U^{(')} \\ S^E &= S^s - S^{(')} - S^{(')} \\ V^E &= V^s - V^{(')} - V^{(')} \\ n_i^E &= n_i^s - n_i^{(')} - n_i^{(')} \end{aligned} \quad (30a, b, c, d)$$

On inserting these definitions and Eqs. (29) into Eq. (28b) Gibbs' adsorption law is obtained as

$$-A \delta\gamma = S^E \delta T - V^E \delta p + \sum_i n_i^E \delta\mu_i^b \quad (31)$$

By choosing, following the procedure of Gibbs, $V^{(')}$ and $V^{('')}$ to make the excess quantities V^E and n_1^E equal to zero, only independent variables are retained in this equation. Then the definitions of the excess functions may be considered to imply that the actual properties of the system are compared to the properties of a hypothetical system with the volume $V^s = V^{(')} + V^{('')}$ in which the homogeneous phases extend to a geometric surface, situated in such a manner as to make n_1^E equal to zero. It can be shown that $S^E, n_2^E, \dots$ thus defined have the same values as the *relative* excess functions vis-à-vis component 1 which are invariant with respect to the positioning of the dividing surface.⁹ Although the above-mentioned choice of independent variables is often advantageous, in some connections it may be more convenient to consider, e.g., $T, p, \mu_3^b, \dots$ ¹⁰ It should be noticed that a deduction of Gibbs' adsorption law could be performed along the same lines by considering a surface phase which in addition contains parts of the homogeneous bulk phases. This is because contributions to the excess functions are only obtained for the physical surface phase when these functions are defined so that two differential coefficients in Eq. (31) vanish. The validity of Gibbs' adsorption law has been investigated experimentally by, for example, the microtome technique of McBain and radio-tracer methods. The accuracy of these and other experiments is, however, scarcely conclusive.

V. THE ENERGY DIFFERENTIAL FOR A NONEQUILIBRIUM SURFACE SYSTEM

If, initially, chemical reactions (*c*), exchange (*e*), and transfer (*tr*) reactions occur within the system, the corresponding affinities A multiplied by the associated increments of the extents of the reactions have to be added to the right-hand side of Eq. (12). The result is

$$dU = T dS - p dV + \gamma dA - \sum_{i=1}^{k-1} A_i^{e'} d\xi_i^{e'} - \sum_{i=1}^k A_i^{tr} d\xi_i^{tr} - \sum_{p=1}^r A_p^c d\xi_p^c \quad (32)$$

This equation defines γ generally, i.e., also for nonequilibrium systems, as

$$\left(\frac{\partial G}{\partial A}\right)_{T,p,\xi^{e'},\xi^{tr},\xi^e} = \gamma \quad (33)$$

where G stands for $U + pV - TS$. Introducing our basic assumption in a generalized form, viz.,

$$-A^t d\xi^t = \left(\sum_i v_i^t \mu_i^s - \sum_i v_i^{t'} \mu_i' - \sum_i v_i^{t''} \mu_i''\right) d\xi^t = \gamma dA \quad (34)$$

Eq. (32) might also be written

$$dU = T dS - p dV - \sum_{i=1}^k \mathbf{A}_i^{m'} d\xi_i^{m'} - \sum_{i=1}^k \mathbf{A}_i^{m''} d\xi_i^{m''} - \sum_{p=1}^r \mathbf{A}_p^c d\xi_p^c \quad (35)$$

indices m' and m'' referring to the molecular transports reactions (6).

In its most general form this equation simplifies to

$$dU = T dS - p dV + \sum_{i\alpha} \mu_i^\alpha dn_i^\alpha \quad (36)$$

where the index α refers to the different phases b' , b'' , and s . It appears that Eq. (36) implies the validity of Gibbs' fundamental equation for each *separate* phase and that μ_i^α is defined always as

$$\left(\frac{\partial G^\alpha}{\partial n_i^\alpha}\right)_{T,p,n_{j\neq i}} = \mu_i^\alpha \quad (37)$$

where $G^\alpha = U^\alpha + pV^\alpha - TS^\alpha$. One may also conclude from this exposition that the frequently cited energy differential expression

$$dU = T dS - p dV + \gamma dA + \sum_i \mu_i^b dn_i \quad (38)$$

is only applicable when equilibrium with respect to exchange and transfer reactions is established, i.e., when $\mathbf{A}_i^{e'} = 0$ and $\mu_i' = \mu_i'' = \mu_i^b$.

VI. BASIC ASSUMPTIONS MADE IN OTHER TREATMENTS

Characteristic features of Gibbs' treatment of surface effects are the introduction of excess functions and the confinement of the theory to equilibrium systems with independent components. Gibbs in the first place considered the variation of the energy U^s

at arbitrarily chosen, but *constant*, boundaries which lie *entirely* beyond the influence of the discontinuity, i.e., at a given volume V^s , area A , and curvature, and he presupposed that δU^s in this case is given by

$$\delta U^s = T \delta S^s + \sum_i \mu_i^s \delta n_i^s \quad (39)$$

By applying the equilibrium condition $(\delta U)_{S,V,n_i} \geq 0$ to the surface phase, subject to these restraints, and the surroundings (which may be taken as all the rest of the system), he demonstrated that T and μ_i^s in Eq. (39) each have the same values as in the homogeneous phases.¹¹ The volume V^s which Gibbs considered is obviously not the actual volume of the region of inhomogeneity since it also contains parts of the homogeneous phases. Because our aim here is to scrutinize only Gibbs' physico-chemical equilibrium condition at planar interfaces, we may instead apply the equilibrium condition $\delta G \geq 0$ at constant T , p , n_i and area, regarding δG^s as given by

$$\delta G^s = \sum_i \mu_i^s \delta n_i^s \quad (40)$$

for these constraints. For equivalence with Gibbs' deduction it would then be required that all n_i^s could be varied independently of each other. However, provided that the physical surface phase is considered, the conditions of constant area, temperature and pressure imply that a relation $\delta A = \sum_i A_i \delta n_i^s = 0$ exists, where A_i denotes a suitably defined partial molar area. Only those combinations of δn_i^s that fulfil this condition may then really occur. Consequently, the k molecular transport reactions (7) cannot proceed independently, but only the $k-1$ equilibrium exchange reactions (3). With any other choice of surface phase boundaries, this restriction is applicable only to the inhomogeneous region and then all n_i^s may be varied independently because for the homogeneous phases there are, of course, no "area" conditions. From this discussion it must be concluded that Gibbs' deduction of the equilibrium condition for a surface system does not necessarily imply that the chemical potential of a substance in a *physical* surface phase equals μ_i^b , but it is required that, when $\delta A = 0$, the condition $\sum_i \mu_i^s \delta n_i^s - \sum_i \mu_i^b \delta n_i^s \geq 0$ shall be separately fulfilled for each independent exchange reaction (cf. Eq. 15). Gibbs in

principle obtained Eq. (27) by adding $-pV^s + \gamma \delta A$ to Eq. (39). It is evident both that our treatment is consistent with the procedure of Gibbs and that all the n_i^s variables are generally independent *except* for the case (which Gibbs excluded) when the boundaries of the physical surface phase are taken as the boundaries of the volume V^s .

Van der Waals, Jr., and Bakker,¹² Verschaffelt,¹³ and Guggenheim³ have developed a treatment of a planar surface system in equilibrium in which the introduction of excess functions is avoided. The aim has apparently been to obtain results more closely related to reality than the Gibbs formulae. In their treatment the fundamental equation (27) results from a detailed consideration of the forces acting on a surface phase, and it is shown that the work required to alter the surface area at a *constant material content* in the surface phase equals $-p dV^s + \gamma dA$, implying that A and all the n_i^s are regarded as independent variables. *A priori*, it is assumed that the temperature, pressure, and chemical potentials have the same values throughout the system at equilibrium. However, similar arguments as those used above may also be applied here. Thus, if the boundaries of the surface phase under consideration are also the boundaries of the physical surface phase, no means in general exist which make it possible to increase the surface area at a fixed material content, because a physical surface phase cannot, without a change of its properties, be separated from the adjacent bulk phases. The converse, i.e., our assumption that a variation of the surface area is followed by a transport of substances to the surface phase, appears to be more adequate. When the boundaries of the surface phase are positioned somewhere outside the physical surface phase (as in the above-mentioned authors' treatments), an increase in the surface area at a constant material content may really be performed, e.g. by introducing separating walls between the surface phase and the bulk phases, and therefore the area A and the n_i^s variables are independent in this case. This state of affairs implies that if the partial derivative of $G^s = U^s + pV^s - TS^s$ with respect to n_i^s is calculated from Eq. (27) as

$$\left(\frac{\partial G^s}{\partial n_i^s}\right)_{T,p,n_j^s,A} = \mu_i^b \quad (41a)$$

the relation obtained is physically meaningful only for a surface phase which includes homogeneous regions but not for the physical surface phase.

Several authors have stated that there would be a correspondence between pV -work and surface work and have therefore considered $G^s - \gamma A$ as the Gibbs' free energy function for the surface phase. Such an approach is legitimate when the surface phase considered includes bulk-phase regions because we may derive (leaving out subscripts T and p) the equation

$$\begin{aligned} \mu_i^b = \left(\frac{\partial(G^s - \gamma A)}{\partial n_i^s} \right)_{n_j^s, \gamma} &= \left(\frac{\partial G^s}{\partial n_i^s} \right)_{n_j^s, A} \\ &+ \left(\frac{\partial G^s}{\partial A} \right)_{n_i^s} \left(\frac{\partial A}{\partial n_i^s} \right)_{n_j^s, \gamma} - \gamma \left(\frac{\partial A}{\partial n_i^s} \right)_{n_j^s, \gamma} \end{aligned} \quad (41b)$$

and this relationship is adequate when treating a surface phase for which $(\partial G^s / \partial A)_{T, p, n_i^s}$ can be put equal to γ .

Defay and Prigogine⁹ have, following de Donder,¹⁴ shown that the energy differential for a planar surface system which is not in equilibrium with respect to adsorption and chemical reactions should be written

$$\begin{aligned} dU = T dS - p dV + \gamma dA \\ - \sum_{i=1}^k \mathbf{A}_i^{a'} d\xi_i^{a'} - \sum_{i=1}^k \mathbf{A}_i^{a''} d\xi_i^{a''} - \sum_{p=1}^r \mathbf{A}_p^c d\xi_p^c \end{aligned} \quad (42)$$

Here $\xi_i^{a'}$ and $\xi_i^{a''}$ are the extents of adsorption reactions which imply an independent transport of each constituent to the Gibbs' geometrical surface from the bulk phases b' and b'' such that $dn_i^E = d\xi_i^{a'} + d\xi_i^{a''}$. Gibbs' surface system model is used and the surface phase considered also contains parts of the homogeneous phases. Therefore no direct comparison between Eqs. (32) and (42) is possible. The last-mentioned equation cannot, however, be in contradiction to our assumptions because the regarded surface phase also contains homogeneous masses; it represents instead an alternative way of extending the theory to non-equilibrium systems.

Butler² regarded the energy differential for a monolayer as being given by Eq. (25) and showed that this equation is consistent with the Gibbs' theory, pointing out that Gibbs' deduction does not necessarily give any information as to the value of μ_i^s . The exchange reactions were not introduced, but in several other respects his treatment follows the same general lines as the present one. Since only monolayers were considered, however, it may not be regarded as quite general.

VII. THE SURFACE PHASE TREATED AS A SERIES OF HOMOGENEOUS SUBPHASES

It is universally recognized that Gibbs' theory of capillarity possesses the merit that it does not contain any assumption regarding the structure of the surface phase. This could be achieved with the aid of the surface system model introduced and the surface excess functions. As will now be shown, it seems possible to introduce the structure in a rather general way if Eq. (21) is utilized. Since, *a priori*, by ordinary thermodynamic means, nothing can be stated concerning the magnitude of the actual surface layer thickness τ in relation to the molecular dimensions, it appears to be appropriate to investigate the properties of a surface phase by regarding it as consisting of a number of equally thin, approximately uniform subphases. By proceeding in this way, structural information may in principle be obtained through comparison with experimental data. The l th layer is supposed to contribute γ_l to the surface tension. By analogy with Eq. (21), we may then write

$$\sum_i (\mu_i^l - \mu_i^b) \delta n_i^l = \gamma_l \cdot \delta A \quad (43)$$

This equation may be integrated at constant temperature, pressure, and composition, corresponding physically to a building-up of the systems' area at constant surface tension. Thus we get

$$\sum_i (\mu_i^l - \mu_i^b) n_i^l = \gamma_l \cdot A \quad (44)$$

Summation over the whole surface phase leads to

$$\sum_l \sum_i (\mu_i^l - \mu_i^b) n_i^l = \gamma \cdot A \quad (45)$$

It now appears that it is convenient to regard μ_i^s as a *mean value* of μ_i^l in the surface layer:

$$\mu_i^s = (\sum_l \mu_i^l n_i^l) / \sum_l n_i^l \quad (46)$$

If use is made of this definition, Eq. (45) becomes

$$\sum_i (\mu_i^s - \mu_i^b) n_i^s = \gamma \cdot A \quad (47)$$

because $\sum_l n_i^l = n_i^s$. For a surface phase in equilibrium we get the result that the sum of all the equations (43) may be written

$$\sum_i (\mu_i^s - \mu_i^b) \delta n_i^s = \gamma \delta A \quad (48)$$

because $\delta n_i^l / \delta n_i^s = n_i^l / n_i^s$. Consequently, the Gibbs–Duhem equation is also fulfilled for the surface phase since it appears that

$$\sum_i n_i^s \delta \mu_i^s = \sum_l \sum_i n_i^l \delta \mu_i^l \quad (49)$$

and for each approximately uniform layer the Gibbs–Duhem equation should hold. According to Eq. (44) the effective surface layer thickness τ is given by $\tau = \delta(\omega + 1 - \alpha)$, where δ is the distance between the equidistant planes. For $l = \omega + 1$ and $l = \alpha - 1$ the equation $\mu_i^l - \mu_i^b = 0$ holds approximately true for all i , i.e. $\gamma_l = 0$, but not when $l = \omega$ and $l = \alpha$. Thus n_i^s may be regarded as determined by

$$n_i^s = \sum_{l=\alpha}^{\omega} n_i^l.$$

In an analogous manner, a mean molar volume v_i^s may be defined which at constant T and p fulfils the relationships

$$\sum_i n_i^s v_i^s = V^s \quad \sum_i v_i^s \delta n_i^s = \delta V^s \quad (50a, b)$$

Now A is equal to V^s/τ and we therefore have

$$\sum_i n_i^s A_i = A \quad \sum_i A_i \delta n_i^s = \delta A \quad (51a, b)$$

where $A_i = v_i^s/\tau$ is a partial molar area associated with the i th constituent. Only in the case of a monolayer, obviously, does A_i correspond to the projected area of the molecular volume. Equation (51b) strictly holds true when T and p are held constant. However, it may often be assumed that the effect of temperature

and pressure in this connection is negligible—an assumption that is consistent with the basic ideas in the present treatment. Hence, the application of Eq. (51b) at non-prescribed restraints at least represents a good approximation.

VIII. THE GENERAL ADSORPTION LAW

We have pointed out above that, for an equilibrium surface system, the affinities for all exchange and transfer reactions are zero. This condition may be written according to Eq. (15) as

$$-\mathbf{A}_i^e = v_{ii}^e(\mu_i^s - \mu_i^b) - v_{i+1,i}^e(\mu_{i+1}^s - \mu_{i+1}^b) = 0 \quad (52)$$

$$(i = 1, 2 \dots k - 1)$$

But the stoichiometric coefficients should obey the relationship [cf. Eq. (5)]

$$v_{ii}^e A_i = v_{i+1,i}^e A_{i+1} \quad (i = 1, 2 \dots k - 1) \quad (53)$$

because every independent exchange reaction characterizes of the property that it occurs at constant surface area. Hence we may write

$$\text{const.} = (\mu_i^s - \mu_i^b)/A_i = (\mu_{i+1}^s - \mu_{i+1}^b)/A_{i+1} \quad (54)$$

$$(i = 1, 2 \dots k - 1)$$

Combining Eqs. (54) and (13) gives the result

$$\mu_i^s - \mu_i^b = A_i \gamma \quad (i = 1, 2 \dots k) \quad (55)$$

since $dA = \sum_i v_i^t A_i d\xi^t$. Another way of deducing the equilibrium condition (55) is to combine Eqs. (21) and (51), leading to

$$\sum_i (\mu_i^s - \mu_i^b - A_i \gamma) \delta n_i^s = 0 \quad (56)$$

As all δn_i^s in this equation should be regarded as independent (cf. Section (III)), this equation generally holds true only if the condition (55) is satisfied. Equation (55) may be regarded as a general adsorption law since it enables us to account for a variety of surface phenomena, as will be shown subsequently. The same equation was, using similar arguments, first derived by Butler² for the monolayer case. Defay and Prigogine⁹ and Kofoed and Villadsen⁵ later deduced similar equations on other grounds.

Equation (55) also suggests the introduction of the name surface-chemical potential for μ_i^s thus underlining the facts that μ_i^s enters into the fundamental equation for a surface phase in the same manner as μ_i^b enters into the corresponding equation for a bulk phase and that generally $\mu_i^s \neq \mu_i^b$. In these respects μ_i^s is analogous to the electrochemical potential. However, the counterpart of Eq. (55) in the thermodynamics of electrochemical systems is the well-known relation

$$\mathbf{A}_g = n_g F E \quad (57)$$

where E denotes the electromotive force and $\mathbf{A}_g$ refers to the g th cell reaction.

In order to make our main equation useful for dealing with experimental data, it is necessary to introduce variables other than the chemical potentials. According to Lewis, the activity of a component in a uniform phase may be introduced by

$$\mu_i^b = \mu_i^{0b} + RT \ln a_i^b \quad (58)$$

and the activity a_i^l is *per analogia* given by

$$\mu_i^l = \mu_i^{0l} + RT \ln a_i^l \quad (59)$$

From the definition of μ_i^s as a mean value it follows that

$$\mu_i^s = \sum_l (\mu_i^l n_i^l) / n_i^s = \sum_l \mu_i^{0l} q_i^l + RT \sum_l q_i^l \ln a_i^l \quad (60)$$

where q_i^l equals the quotient n_i^l / n_i^s . Introducing $q_i^{0l} = n_i^{0l} / n_i^{0s}$, index 0 denoting the properties of the pure substance, we may now write

$$\mu_i^s = \mu_i^{0s} + RT \sum_l q_i^{0l} [(\mu_i^{0l} / RT)(1 - q_i^{0l} / q_i^l) + \ln a_i^l] \quad (61)$$

because $\mu_i^{0s} = \sum_l \mu_i^{0l} q_i^{0l}$ is a constant which does not depend upon the composition. The pure substance is thus conveniently taken as the standard state. Since the quantity $(\mu_i^{0l} / RT)(1 - q_i^{0l} / q_i^l)$ has the dimension zero and vanishes for the standard state, we may regard the structural factor φ_i^l , defined by

$$\ln \varphi_i^l = (\mu_i^{0l} / RT)(1 - q_i^{0l} / q_i^l) \quad (62)$$

as a correction factor of a similar nature to an activity factor. Combining Eqs. (61) and (62) we get

$$\mu_i^s = \mu_i^{0s} + RT \ln \prod_l (a_i^l \varphi_i^l)^{q_i^l} \quad (63)$$

Since $\prod_l (x_i^s)^{q_i^l} = x_i^s$, the total activity factor in the surface phase is conveniently defined as

$$f_i^s = \prod_l [f_i^l \varphi_i^l (x_i^l/x_i^s)]^{q_i^l} \quad (64)$$

where $f_i^l = a_i^l/x_i^l$ and x stands for mole fraction. The activity factor f_i^s consequently reflects not only variations in the intra-molecular interaction but also in the structural arrangement of the surface phase. Only in the case of a homogeneous surface phase is the structure of no importance, as is readily evident. For a monolayer, in particular, f_i^s equals f_i^1 . Now it may be stated that

$$\mu_i^s = \mu_i^{0s} + RT \ln f_i^s x_i^s \quad (65)$$

where it should be remembered that although f_i^s has partly the same general properties as an activity factor it also depends on the structure of the surface layer. Combining Eqs. (55), (58), and (65) leads to

$$\ln f_i^s x_i^s / f_i^b x_i^b = (A_i \gamma - A_i^0 \gamma_i^0) / RT \quad (66)$$

where use has been made of the fact that the pure substance is the standard state, i.e.,

$$\mu_i^{0s} - \mu_i^{0b} = A_i^0 \gamma_i^0 \quad (67)$$

A mathematically equivalent form of Eq. (66) is

$$x_i^s/x_i^b = F_i e^{(A_i \gamma - A_i^0 \gamma_i^0)/RT} \quad (68)$$

where F_i denotes the quotient of the activity factors, viz., f_i^b/f_i^s . An equation similar to Eq. (66) was first derived by Butler² assuming a monolayer arrangement and $A_i = A_i^0$. Later, Hoar and Melford,¹⁵ not using the concept of chemical potential but instead regarding γ as the total free energy of the system per unit area, i.e., considering that $(\partial G/\partial A)_{T,p} = \gamma$, succeeded in deducing (66) for the case of a binary system without having to use $A_i = A_i^0$.

IX. THE SURFACE TENSION OF LIQUID MIXTURES

A. General

In the following section we shall investigate the variation of the surface tension with the composition of the liquid bulk phase (b') and of the surface phase (s) for liquid-gas systems. Since we have k constituents, there are k equilibrium conditions (55). In addition, the relations

$$\sum_i x'_i = 1 \quad \sum_i x^s_i = 1 \quad (69a, b)$$

must be satisfied. Thus,

$$\sum_i x'_i F_i \exp (A_i \gamma - A_i^0 \gamma_i^0) / RT = 1 \quad (70)$$

For a binary mixture, we have

$$x'_1 F_1 e^{\Delta g_1} + x'_2 F_2 e^{\Delta g_2} = 1 \quad (71)$$

where $\Delta g_i = (A_i \gamma - A_i^0 \gamma_i^0) / RT$. The surface tension varies with the surface molar fraction according to

$$\sum_i (x^s_i / F_i) e^{-\Delta g_i} = 1 \quad (72)$$

An ideal surface phase may be characterized by the criteria $f^s_i = 1$ and $A_i = A_i^0$. It is obvious that these conditions imply that the surface phase is both uniform and ideal in the ordinary sense and in addition that τ is a constant. From Eqs. (69) and (71), we may deduce that for an ideal binary system the following inequality always holds if $\gamma_1^0 > \gamma_2^0$

$$\gamma_1^0 \geq \gamma \geq \gamma_2^0 \quad (73)$$

B. The Experimental Verification of Eq. (71)

Due to the work of Schuchowitsky, Belton and Evans, Guggenheim, Prigogine and Defay based on statistical thermodynamics, it is well known that a formula of the form of Eq. (71) may predict the surface tension of a binary liquid mixture. The main difficulty inherent in its application is the evaluation of the quantities f^s_i and A_i . Hoar and Melford¹⁵ measured the surface tension for the systems tin-lead and indium-lead and showed that among various other suggested formulae Eq. (71) best fitted

the experimental data, provided A_i was calculated as the area occupied by the molecule in a close-packed monolayer and f_i^s was estimated from the theory of regular mixtures. The present author has used a somewhat different method when applying Eq. (71) to the systems $\text{H}_2\text{O}-\text{CH}_3\text{OH}$, $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$, $\text{H}_2\text{O}-\text{HCOOH}$, and $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$. From Eq. (71) we find that for $x'_2 = 1$

$$d\gamma/dx'_2 = (RT/A_2^0)(1 - F_1 e^{\Delta g_1}) \quad (74)$$

if it is assumed that $(dF_2/dx'_2) = 0$ when $x'_2 = 1$. Consequently, when $\gamma_1^0 > \gamma_2^0$, the slope of the surface tension curve for $x'_2 = 1$ is mainly a measure of A_2^0 , because $\exp \Delta g_1 \ll 0$. The value of A_2^0 thus obtained was used as a starting value for the fitting of Eq. (71) at various compositions with respect to A_1^0 and A_2^0 assuming F_1 and F_2 to be unity and the variation of the molar areas with concentration to be negligible. The best trial calculations and their comparison with experimental points are shown in Figs. 1 and 2. The molar areas obtained show, indeed, that the monolayer description is a good one, because it is known that a water molecule in the ideal ice structure occupies an area of $17.6 \text{ \AA}^2$ ¹⁸ whereas the present calculation gives $17 \text{ \AA}^2$ /molecule for all four systems.

The deviations from the theoretically predicted behavior are rather small for the systems $\text{H}_2\text{O}-\text{CH}_3\text{OH}$, $\text{H}_2\text{O}-\text{HCOOH}$, and $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$. In the case of $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$, however, the experimental points could not be fitted to a single curve. As may be inferred from Fig. 2, the area associated with the ethyl alcohol molecule varies between $43 \text{ \AA}^2$ and $75 \text{ \AA}^2$. An explanation of this behavior may be attempted along the following lines. At low alcohol concentrations the water structure of the solution in bulk is fairly undisturbed, thus providing a sufficiently well ordered substrate for the formation of a dense and well arranged surface film in which the alcohol molecules are preferentially parallel to each other and approximately perpendicular to the surface. In this state, the area required per molecule is small. At high alcohol concentrations, the water structure is strongly disturbed by the hydrocarbon chains, thus providing a poor substrate for the formation of the surface film which appears as an expanded, disarranged phase of increased molecular area due to thermal motion and imperfect orientation of the carbon chains. It is interesting

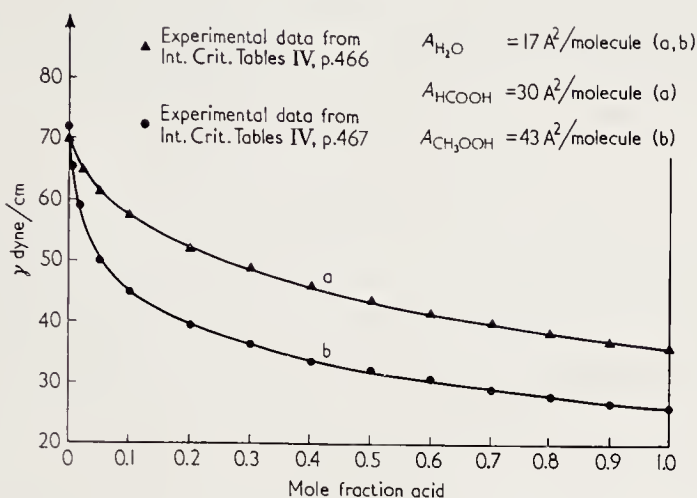


Fig. 1. Calculated and experimental surface tension of the systems $\text{H}_2\text{O}-\text{HCOOH}$ (a) and $\text{H}_2\text{O}-\text{CH}_3\text{COOH}$ (b).

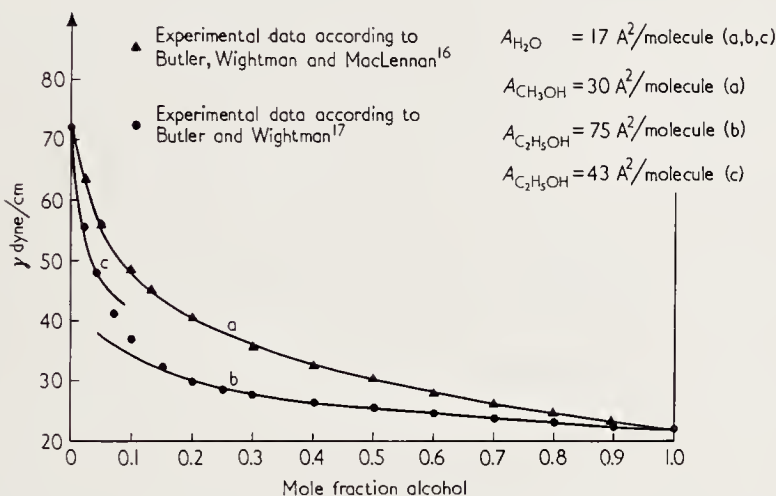


Fig. 2. Calculated and experimental surface tension of the systems $\text{H}_2\text{O}-\text{CH}_3\text{OH}$ (a) and $\text{H}_2\text{O}-\text{C}_2\text{H}_5\text{OH}$ (b, c).

to note that the molecular areas of acetic acid and ethyl alcohol are equal in the low concentration range, showing that the disturbing effect of the short hydrocarbon chain of the acetic acid molecule is small compared to that of the ethyl alcohol. However, this discussion is only tentative since the actual course of the γ - x -curve may also indicate that the assumptions $F_1, F_2 = 1$ are inadequate.

C. Derivation of Szyszkowski's Formula. Traube's Rule

Szyszkowski¹⁹ established the empirical relationship

$$1 - \frac{\gamma}{\gamma_1^0} = C \log \left(1 + \frac{c_2}{a} \right) \quad (75)$$

valid for dilute solutions of some fatty acids in water, c_2 denoting the bulk-phase concentration of the acid in mole/l. C is a constant equal to 0.411 for all the acids investigated, but the a -value depends on the number of carbon atoms in the acid molecule. It will now be shown that Eq. (75) may be derived from Eq. (71). If ideality is assumed, we have

$$x_1' + x_2' e^{\Delta g_2 - \Delta g_1} = e^{-\Delta g_1} \quad (76)$$

index 1 denoting water and 2 the fatty acid. Since only dilute solutions are considered, we are justified in putting $x_1' = 1$. The second term on the left-hand side of Eq. (76) cannot be neglected because $\exp(\Delta g_2 - \Delta g_1)$ is a large quantity dependent on γ . As a somewhat crude approximation, the nature of which will be further treated below, one may consider a mean value defined by

$$\Delta g_2 - \Delta g_1 \approx 0.5(A_1^0 + A_2^0)(\gamma_1^0 - \gamma_2^0)/RT = \Delta g_m \quad (77)$$

Hence

$$\frac{RT \ln 10}{A_1^0 \gamma_1^0} \log (1 + x_2' \cdot e^{\Delta g_m}) = 1 - \frac{\gamma}{\gamma_1^0} \quad (78)$$

Comparing Eqs. (78) and (75) gives

$$C = RT \ln 10 / A_1^0 \gamma_1^0 = 0.411 \quad (79)$$

thus implying that $A_1^0 = 32 \text{ A}^2/\text{molecule}$. From Eq. (78) it is evident that

$$\Delta g_m = \ln 55.5/a \quad (80)$$

The a -values reported for the acids containing 3, 4, 5, and 6 carbon atoms are 0.165, 0.051, 0.015, and 0.0043 respectively. According to Eqs. (77) and (80), the corresponding molecular areas are 72, 92, 115, and 137 A^2 . Consequently, the so-called Traube's rule,²⁰ stating that the constant a is diminished about three times for every added carbon atom, may be interpreted to be a consequence of an increase in the molecular area of the acid of about

20 A².²¹ It is to be noted that the approximation, $\Delta g_2 - \Delta g_1 = \Delta g_m$, implies the validity of a Langmuir isotherm because

$$(x_2^s/x_2')/(1 - x_2^s) = e^{\Delta g_2 - \Delta g_1} = \text{const.} \quad (81)$$

or

$$x_2^s = \text{const. } x_2'/(1 + \text{const. } x_2') \quad (82)$$

Therefore it is possible to deduce Eq. (82) by combining Eq. (75) and Gibbs' adsorption law. The reader will not fail to observe that the molar areas obtained from Szyszkowski's formula are not necessarily the correct ones. This is because $\Delta g_2 - \Delta g_1 = \text{const.}$ is an approximation and the choice $\text{const.} = \Delta g_m$ is arbitrary. Moreover, it appears from Eq. (75) that the effect of a larger value of C (smaller A_1^0) may be counteracted by a larger a -value (smaller A_2^0) and vice versa. The relative magnitudes of the molar areas seem, however, to be reasonable.

D. The Equation of State for Surface Films

It is well known that the gas law-like formula

$$A(\gamma_1^0 - \gamma) = n_2^s RT \quad (83)$$

is approximately valid for a "gaseous" surface film.²² Most experimental workers have studied films on water (index 1). Since there is, in principle, no difference between a film created by a soluble and a practically insoluble substance, there should be a connection between Eqs. (83) and (72). This is in fact the case, as will now be shown. If the activity factors are neglected, and as the mole fraction of B₂ is extremely small, according to Eq. (72) we have

$$e^{-\Delta g_1} = 1/(1 - x_2^s) \quad (84)$$

because $x_2' = x_2^s e^{-\Delta g_2} \approx 0$. Consequently, if A_1 and A_2 are considered constant, equal to A_1^0 and A_2^0 ,

$$\frac{A_1^0}{RT} (\gamma_1^0 - \gamma) = x_2^s + \frac{(x_2^s)^2}{2} + \frac{(x_2^s)^3}{3} + \dots \quad (85)$$

or, approximately,

$$A_1^0(\gamma_1^0 - \gamma) = \frac{[A - n_2^s(A_2^0 - A_1^0)]}{n_1^s + n_2^s} (\gamma_1^0 - \gamma) = RT x_2^s \quad (86a, b)$$

But, when $n_2^s(A_2^0 - A_1^0) \ll A$, we obtain Eq. (83). The less approximate formula (86b) corresponds to relations which have been widely used. Recently Fowkes,²³ using equivalent arguments, has derived the above equations. Of them, Eq. (84) was shown to give the best agreement with experimental data.

E. Extreme Values of the Surface Tension of Binary Mixtures

For an ideal binary mixture, the derivative of γ with respect to x_2' is found from Eq. (71) to be

$$\frac{d\gamma}{dx_2'} = -\frac{RT}{\bar{A}}(e^{Ag_2} - e^{Ag_1}) \quad (87)$$

where $\bar{A}$ equals the area per mole of the surface-phase mixture. If $\gamma_1^0 > \gamma_2^0$, then according to Eq. (73) we always have $\exp(Ag_2) > \exp(Ag_1)$ and thus no extreme or inflexion point will appear in the surface tension curve. It is possible, however, that a third molecular species can be formed from the two independent components that constitute the mixture due to association, complex or micelle formation, etc. In such a case, Eq. (87) must be replaced by

$$\frac{d\gamma}{dx_2'} = -\frac{RT}{\bar{A}}[e^{Ag_2} - e^{Ag_1} - (dx_3'/dx_2')(e^{Ag_1} - e^{Ag_3})] \quad (88)$$

where the derivative dx_3'/dx_2' may be expressed in terms of x_2' and an equilibrium constant for the complex formation. Since the possibility that the right-hand side of Eq. (88) may become zero is not excluded, one may expect that extreme values sometimes appear for such systems. Thus a maximum or minimum in the surface tension for a binary mixture can be explained either as a deviation from ideality²⁴ or, more probably, as an effect due to complex formation in a wide sense. Conversely, Eq. (88) may perhaps, in certain cases, serve as a mean for estimating the corresponding equilibrium constants. From the experimental work so far performed on this question, it is now normally accepted that an explanation along these general lines is the correct one.

X. ADSORPTION AT LIQUID-GAS AND LIQUID-LIQUID INTERFACES

A. General

It has been presumed here that an adsorption reaction has the character of an exchange reaction. We shall therefore consider in more detail the reaction



which is the only exchange reaction taking place between the liquid bulk phase and the surface phase in the case of a binary system. Since the ratio of the stoichiometric coefficients ν_{11}' and ν_{21}' is given by Eq. (53), we may conveniently introduce an arbitrary, but constant, area A^* defined as

$$\nu_{11}'A_1 = \nu_{21}'A_2 = A^* \quad (90)$$

which determines the absolute magnitude of the stoichiometric coefficients. It appears that A^* is physically equal to the area of the surface phase in which all molecules of B_2 are replaced by B_1 when the exchange reaction proceeds from the left to the right. The equilibrium constant for the exchange reaction is

$$(a_1^s/a_1')^{A^*/A_1} \cdot (a_2'/a_2^s)^{A^*/A_2} = K_1' \quad (91)$$

and it is easily shown, assuming the molar areas to be constant and applying Eq. (52), that

$$(A_1')^0 = -A^*(\gamma_1^0 - \gamma_2^0) = RT \ln K_1' \quad (92)$$

where $(A_1')^0$ is the standard affinity of the exchange reaction. An alternative way of deducing this relation is to eliminate γ between the two relations (68). It is interesting to note that γ_1^0 and γ_2^0 have the same roles in (92) as the standard potentials of electrodes in the corresponding electrochemical relation. Likewise, Eq. (66) may be regarded as analogous to the Nernst formula. The standard heat of the exchange reaction can now be calculated using

$$\frac{d \ln K_1'}{dT} = \frac{(\Delta H_1')^0}{RT^2} \quad (93)$$

Hence we find

$$(\Delta H_1^e)^0 = A^* \left[\left(\gamma_1^0 - T \frac{d\gamma_1^0}{dT} \right) - \left(\gamma_2^0 - T \frac{d\gamma_2^0}{dT} \right) \right] \quad (94)$$

in agreement with the fact that for the pure substances

$$(\Delta H_i^m)^0 = A_i \left(\gamma_i^0 - T \frac{d\gamma_i^0}{dT} \right) \quad (95)$$

as was first shown by Lord Kelvin²⁵ in 1858.

B. Langmuir's Adsorption Formula

According to Eq. (91) we have in the case of ideality, choosing $A_1^0 = A_1^*$

$$(x_1^s/x_1')[(1 - x_1')/(1 - x_1^s)]^{A_1^0/A_2^0} = K_1^{e'} \quad (96)$$

When B_1' is adsorbed at the surface and $x_1' \ll 1$

$$(x_1^s/x_1')(1 - x_1^s)^{-A_1^0/A_2^0} = K_1^{e'} \quad (97)$$

is a reasonable approximation. Furthermore, as long as x_1^s is small, Eq. (97) may be approximated through a series expansion. We then get

$$x_1^s = K_1^{e'} x_1' / [1 + K_1^{e'} (A_1^0/A_2^0) x_1'] \quad (98)$$

which represents the Langmuir isotherm. When $x_1' = p_1/p_1^0$ this isotherm can also be written in the more familiar form

$$x_1^s = ap_1/(1 + bp_1) \quad (99)$$

a and b denoting constants. The above derivation is valid for adsorption from a gaseous or a liquid bulk phase at a liquid surface. However, the adsorption at solid interfaces may also, in principle, be described by exchange reactions, but theoretical complications arise owing to the restricted mobility of molecules in the solid state.

XI. SURFACE EQUILIBRIA

Consider the case when chemical equilibrium between some constituents is established within the system. Let us consider the independent equilibrium reaction

$$\sum_i \nu_{i,p}^c B_i^b = 0 \quad (100)$$

The equilibrium condition is obviously

$$\sum_i \nu_{i,p}^c \mu_i^b = 0 \quad (101)$$

or

$$\sum_i \nu_{i,p}^c (\mu_i^s - A_i \gamma) = 0 \quad (102)$$

On introducing activities and standard chemical potentials, we obtain

$$RT \ln K_p^{c,s} = -\sum_i \nu_{i,p}^c \mu_i^{0s} + \gamma \sum_i \nu_{i,p}^c A_i \quad (103)$$

But from Eq. (101)

$$RT \ln K_p^{c,b} = -\sum_i \nu_{i,p}^c \mu_i^{0b} \quad (104)$$

Combining Eqs. (103) and (104) gives

$$\ln K_p^{c,s}/K_p^{c,b} = (1/RT) \sum_i \nu_{i,p}^c (A_i \gamma - A_i^0 \gamma_i^0) \quad (105)$$

where use has been made of Eq. (67).

Hence

$$\ln K_p^{c,s}/K_p^{c,b} = \sum_i \nu_{i,p}^c A_i g_i \quad (106)$$

Thus we conclude that, in general, the position of the equilibrium in a surface phase is *not* the same as in a bulk phase. From Eq. (106) it also appears that the quotient $K_p^{c,s}/K_p^{c,b}$ is altered in such a way as to favor the formation of compounds with a low surface tension. Butler² was the first to describe this situation quantitatively, using similar arguments, and pointed out that Eq. (106) is equivalent to the statement of J. J. Thomson²⁶ that "if the surface tension increases as the chemical action goes on the capillarity will tend to stop the action, while if the surface tension diminishes as the action goes on, the capillarity will tend to increase the action". Experimental evidence supporting these conclusions has been presented.²⁷

XII. CONCLUSIONS

From the present treatment it may be concluded that it is appropriate to develop a thermodynamics for surface systems which relies upon considerations of the physical surface phase, because the given approach apparently implicates a useful and unifying basis for predicting the behavior of many surface systems. In this paper, problems related to the surface tension of mixtures, adsorption, surface films and surface equilibria have been treated. Recently, by applying the derived formula to experimental data, the author has demonstrated that Eq. (55) is also a convenient starting-point when studying the effect of pressure on the surface tension of binary liquid-gas systems.²⁸ Thus, notwithstanding the possibility that doubts might be raised on theoretical grounds about the applicability of nonstatistical thermodynamics to the physical surface phase, which is known to have a thickness of atomic dimensions, the present theory displays a remarkably satisfactory agreement with experiment. There are also conceptual advantages connected with the approach since the introduction of excess functions is superfluous. Likewise, the usual definition of the Gibbs' free energy function can be retained. However, it has been assumed that an increase of the surface area is *always* connected with a transport of substances to the physical surface phase. Such an assumption comprises an approximation because, generally,

$$\delta A = \left(\frac{\partial A}{\partial T} \right)_{p, n_i^s} \delta T + \left(\frac{\partial A}{\partial p} \right)_{T, n_i^s} \delta p + \sum_i A_i \delta n_i^s \quad (107)$$

$$\delta A = \sum_i A_i \delta n_i^s + \sum_i n_i^s \delta A_i \quad (108)$$

Consequently δA equals $\sum_i A_i \delta n_i^s$ only for variations at constant T and p . But often the effects of temperature and pressure changes on the partial molar surface areas are negligible so that $\sum n_i^s \delta A_i = 0$ holds approximately true under all conditions. The perfectly general treatment along these lines should obviously take into account the exact equations (107) and (108). However, as may readily be verified, no essential modifications of the conclusions obtained here would then be required.

In order to achieve a more complete understanding of the basic postulate in this treatment, i.e., that it is possible to account for the surface work by presupposing that the chemical potentials in bulk and in the surface phases have different values, further investigations should be performed in which the fact that a physical surface phase is subject to a nonisotropic stress has to be considered in detail.

XIII. ACKNOWLEDGEMENTS

The author is much indebted to the Head of the Division, Professor Ole Lamm, who initiated this work and who has, through many stimulating discussions, contributed considerably to its advancement. Thanks are due also to Dr. E. Forslind for valuable comments and advice. Dr. A. Rupprecht and Mr. B. Söderqvist are thanked for helpful discussions.

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THE CRITICAL REGION*

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I. INTRODUCTION

To review even the more significant work that bears on the critical region would require an encyclopedic exposition of many-body physics, and the author is so far from being capable of such an exposition that he will not be chastised for failing in what he has not attempted. The present review focuses on the author's own work, and experiment and other theories are brought in mainly to sketch the tree from which this branch grows.

* Supported in part by the National Science Foundation and the Division of General Medical Sciences, Public Health Service.

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The mathematical and physical theory of equilibrium cooperative phenomena in crystals has been reviewed by Newell and Montroll,⁸⁶ and Domb,²⁴ and the basic statistical mechanics is reviewed in Hill's monograph.⁴⁸ Rowlinson¹⁰⁸ has given a very thorough discussion of the classical thermodynamics of the coexistence curve and the critical region, and has also appraised much of the better data on equilibrium properties (of liquids and liquid mixtures). Rice^{102,103} has several times reviewed the field of critical phenomena.

Our present experimental knowledge of either equilibrium or nonequilibrium properties of the critical region is in a rapidly moving state, and the same is true of approximate statistical-mechanical theories of the critical region. The major recent progress in the "exact" theory has come from series extrapolation schemes, and this work has so far been confined to equilibrium properties. If the goal of statistical-mechanical theory is solely the numerical evaluation of the partition function and its derivatives, these extrapolation schemes seem at present the surest road to progress. Other goals, perhaps illusory, have motivated the author's work: namely the abstraction of simple but useful models and the treatment of irreversible processes. A brief discussion of the coexistence curve is our point of departure.

The author would like to acknowledge specific corrections and more general comments received from M. E. Fisher, T. L. Hill, O. K. Rice, and G. S. Rushbrooke.

II. THE COEXISTENCE CURVE

A. Classical Thermodynamics

Every serious student of fluids will own a copy of Rowlinson's book on liquids and liquid mixtures,¹⁰⁸ and there is no warrant for a repetition of his scholarly and lucid exposition of the classical thermodynamics of the critical state. But a few of the important points must be brought to mind. Consider the classical isotherm portrayed in Fig. 1. The solid line represents the observed pressure of a system in its most stable state of volume V . Between points 1 and 4 the compressibility of the fluid is infinite, although approximate statistical-mechanical theories, when based on the canonical ensemble, give a loop between points 1 and 4 and

indicate that the isotherm should follow the dotted line 1,2,3,4.⁴⁸ The first of these approximate theories was that of van der Waals, but the loop seems to occur in any theory which does not allow for the possibility that the system exists in two macroscopic states of different density. If P can be represented by such a continuous and differentiable function of V , then the points of

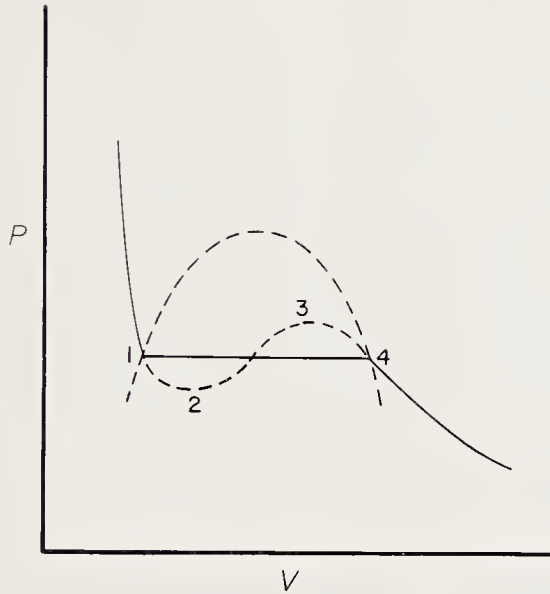


Fig. 1. A van der Waals gas; isotherm and coexistence curve.

phase separation can be determined from the requirement that P and the chemical potential μ be the same at both ends of the tie line, that is at points 1 and 4. The equality of chemical potentials is just the equal area criterion of Maxwell. Suppose that for some temperature below the critical temperature the power series, where ρ is the number density,

$$P - P_0 = \sum_{n=1}^{\infty} \left(\frac{\partial^n P}{\partial \rho^n} \right)_{\rho_c, T} \frac{(\rho - \rho_c)^n}{n!} \quad (1)$$

can be constructed and has a finite radius of convergence. It will be understood that this series has no meaning in conventional statistical mechanics, since it describes unstable and metastable systems. In the exact canonical and grand canonical ensembles,

the region under the coexistence curve will be described only by tie lines.⁴⁸ However, even an approximate grand ensemble will give tie lines.

Whether there exists some modification of exact statistical mechanics which will furnish the loop and a series of the form given in Eq. (1) is a very interesting but unanswered question. An *ad hoc* modification is usually not difficult to find. In the theory of the Ising lattice, for example, the evaluation of the partition function requires the largest eigenvalue of a matrix to be determined. This largest eigenvalue is, in the conventional formulation, degenerate for $T < T_c$, the onset of degeneracy accompanying the onset of long-range order. In an approximate theory, such as the variational theory of Kramers and Wannier,⁵⁹ it seems very probable that a loop would result if the trial eigenfunctions were restricted to those which lack long-range order. In practice, this restriction would exclude their use of a trial function dependent on the total dipole moment of the system. More generally, one can speculate that the loop would derive from a partition function which, when expressed as the trace of a matrix, is calculated with the exclusion of degenerate states.

In the present context, it must be true that at least the first two derivatives on the right-hand side of Eq. (1) vanish at the critical temperature. Zimm¹⁴¹ has speculated that all the derivatives vanish at the critical point. The lowest order nonvanishing derivative must occur for odd n in order that the supercritical state be stable. Suppose that the lowest nonvanishing derivative is the m th and also that the derivatives may be expanded in powers of $T - T_c$. Then near the critical point

$$P - P_0 = \left(\frac{\partial^2 P}{\partial \rho \partial T} \right)_c (T - T_c)(\rho - \rho_c) + \left(\frac{\partial^m P}{\partial \rho^m} \right)_c \frac{(\rho - \rho_c)^m}{m!} \quad (2)$$

The pressure must be the same at points 1 and 4; also

$$\rho^l - \rho_c = -(\rho^g - \rho_c) \quad (3)$$

as follows from the equality of the chemical potentials and every experiment, and therefore

$$-(T - T_c) = \left(\frac{\partial^2 P}{\partial \rho \partial T} \right)_c^{-1} \left(\frac{\partial^m P}{\partial \rho^m} \right)_c \frac{(\rho^l - \rho_c)^{m-1}}{m!} \quad (4)$$

The van der Waals gas will have $m = 3$, and consequently the coexistence curve will have a quadratic top.

Assertions that a quadratic coexistence curve has actually been found are rare,^{60,62} for either liquids or liquid mixtures. Flat-topped curves have been found, cubic curves have been found, and it has definitely been established that $m = 9$ for a square-lattice gas,^{68,69} but the coefficient may not have the classical significance given in Eq. (4).

B. Experimental Problems

Any attempt to settle the shape of the coexistence curve experimentally is beset by severe problems. In the critical state systems attain equilibrium very slowly; this difficulty affects all measurements in the critical region and will be commented on in almost all sections of this work. Another problem for the one-component liquid is the effect of gravity. The effects of impurities are less certain but it has been stated⁷⁶ that the coexistence curve of cyclohexane-aniline has a flat top if the components are dry, but that the addition of a small amount of water can destroy the flat portion (see also Reference 134).

The effects of gravity on the one-component coexistence curve are severe.^{108,112,133,135} In long vertical tubes it is to be expected that large density gradients will occur in the critical region. The effect of these gradients is to cause a flat-topped coexistence curve; if short tubes are used for the measurements, the curves become rounded and, in fact, cubic.

Problems caused by nonequilibrium are extremely difficult to resolve. Wentorf¹³⁴ has asserted that pressure equilibration in the critical region is achieved within 30 min, but that constancy of fluid structure as judged from photographs may require as much as 5 hr. Murray and Mason⁸⁴ found that the turbidity of a critical fluid returned to normal, after compression, within several minutes. The closer the fluid to the critical point the more sluggish are its responses. This difficulty relates particularly to heat-capacity measurements, and will be commented on later, but it should at least be mentioned here that the existence of long-range density correlations is intimately connected with most critical phenomena, and any attempt to stir continuously may destroy these long-range correlations and with them the critical effects.

The flat tops which are found in mixtures^{5,99,104,107} are less easily explained as being due to the effects of gravity, because the composition gradients produced by gravity will be achieved very slowly; diffusion is always a slow process. Zimm¹⁴² has suggested that the data of Rowden and Rice,¹⁰⁷ which were taken to indicate a flat top, may actually be fitted almost as well with a cubic coexistence curve. However, the discrepancies are probably outside experimental error. It should be observed that even though diffusion is slow, the equilibrium concentration gradient can be very large in the critical region. The flux of one component of concentration c in a binary mixture is given by

$$\text{flux} = -D[(\partial\mu/\partial c)_T \nabla c + K\mathbf{g}]$$

where μ is the chemical potential, $\mathbf{g}$ the acceleration of gravity, and K is a constant which measures the difference between the densities of the two components. The flux vanishes at equilibrium and $(\partial\mu/\partial c)_T$ vanishes at the critical point, so if the two components differ in density a very large ∇c may result. It should also be observed that D is nonvanishing at the critical point (see Section VIII), and the flux induced by $\mathbf{g}$ will not be abnormally small. The weight of the experimental evidence^{4,108,140} favors cubic coexistence curves for liquid mixtures, though perhaps not for metallic alloys.⁸³

Attempts have been made to relate the cubic coexistence curve to Eq. (4) with $m = 4$ and $\rho - \rho_c$ replaced by its absolute value.^{105,136} It cannot be said at the moment that this procedure is incorrect, but it sacrifices the differentiability of P with respect to ρ at the critical point without, it appears to the author, a corresponding compensation.

Baker⁶ has recently applied sophisticated numerical methods to low-temperature series expansions of the magnetization of the Ising lattice and deduced the shape of the magnetization curve in the vicinity of the critical point. His results also apply to the three-dimensional lattice gas.⁴⁸ It is found that

$$\rho^l - \rho_c \propto (T_c - T)^{0.3} \quad (5)$$

the error in 0.3 being estimated as, at most, 0.01. Using longer series, M. E. Fisher and J. W. Essam have concluded that the

exponent lies between 0.303 and 0.318, and is probably $5/16$ (private communication). It has thus become almost certain that the cubic curves are not experimental artifacts.

III. RADIAL DISTRIBUTION FUNCTION

A. History

In Einstein's theory of light scattering from fluids,²⁷ it is assumed that the whole scattering volume can be subdivided into small elements of fluid and that the fluctuations of density or composition in these small elements are independent of each other. A consequence of this assumption is that the light scattering becomes infinite at all angles of observation at the critical point. Ornstein and Zernike recognized that the assumption of independent elements of fluid might not be correct in the critical region and were the first to devise a scheme to cope with long-range density correlations. In their paper of 1914⁹² they introduced the concept of a direct correlation function which would be capable of propagating density correlations over a large distance. Their fundamental equation relating the direct correlation function $f(r)$ to the indirect correlation function $G(r)$ has a plausible appearance, even though its derivation is not very convincing. The indirect correlation function is related to the radial distribution function $g(r)$ by $G(r) = g(r) - 1$. It is worth examining their equation for its historical interest.

Ornstein and Zernike characterize $f(r)$ by the statement that

$$G(r) = f(r) \tag{6}$$

if all molecules, except those two which are at the origin and at r , are distributed randomly. But actually, if molecules are fixed at 0 and r , then the distribution of other molecules will not be random; the molecule at r will effect the distribution of molecules at a point $\mathbf{r}_2$ which may be very far away. That altered distribution may have a direct effect on the probability of finding a molecule at the origin. From considerations of this nature, the relation between $G(r)$ and $f(r)$ is asserted to be

$$G(r) = f(r) + \rho \int G(\mathbf{r}_2 - \mathbf{r}) f(r_2) d\mathbf{r}_2 \tag{7}$$

Ornstein and Zernike are then able to develop a van der Waals equation of state by assuming that the interaction energy between all the molecules in two elements of volume is proportional to the numbers of molecules in the two elements. Their famous relationship between the compressibility and $G(r)$ was derived in this connection,

$$(\partial P / \partial \rho)_T = kT \left[1 + \rho \int G(r) d\mathbf{r} \right]^{-1} \quad (8)$$

as was also the connection between density fluctuations and $G(r)$:

$$\langle (N - \bar{N})^2 \rangle = V \left\{ \rho + \rho^2 \int G(r) d\mathbf{r} \right\} \quad (9)$$

From their equation of state they concluded that at the critical point

$$\int f(r) dr = 1 \quad \text{at} \quad \rho_c T_c \quad (10)$$

and furthermore that the angular dependence of light scattering at the critical point required a knowledge of only the one molecular parameter

$$l^2 = \int r^2 f(r) d\mathbf{r} \quad (11)$$

which is a measure of the range of direct correlation.

Shortly afterward,¹³⁹ the equation $G(r) \sim r^{-1} \exp(-\kappa r)$ was first presented as an explicit description of correlations in the critical region. Much of the material was reviewed in 1926,⁹⁴ and in 1930 Placzek⁹⁸ showed that the prediction of infinite scattering into zero angle at the critical point was a consequence of the infinite scattering volume assumed. A finite volume gives finite scattering.

An entirely different line of thought eventually found its way into the theory of critical correlations. In the late nineteenth century it was realized that the treatment of capillary and surface phenomena by continuum mechanics required that the free-energy density depend on the gradient of density or composition, as well as on the density itself. These efforts are reviewed by Bakker,⁷ particularly in Chapter 15. Many years later this work was taken up by Cahn and Hilliard, particularly for its application to nucleation theory, and given a firm thermodynamic foundation by

them and by Hart.^{15,16,17,41} There had been much work in the interim period, with both formal and molecular attacks on the nature of boundary layers and other inhomogeneous systems in equilibrium, particularly by Hill.⁴⁹

Landau was the first to apply these ideas of continuum mechanics to the problem of light scattering from the critical region,^{64,65} or rather to the virtually identical problem of X-ray scattering from crystals near the Curie point. This problem will be reviewed later.

The most elegant and clear exposition of the ideas of Ornstein and Zernike is that of Klein and Tisza.⁵⁸ The ideas of Ornstein and Zernike will be understood to mean generally the assumption of a linear direct (or short-range) coupling between fluctuations of density in different volume elements, in an expression for the free energy in an inhomogeneous system.

The Ornstein–Zernike integral equation reduces to a differential equation for large values of the argument, an equation identical to the wave equation with an imaginary wave number. This differential equation, as will be pointed out in more detail in the next section, is an immediate consequence of the assumption that the free-energy density depends quadratically on the density fluctuation and on the gradient of density, and accordingly the generalization of mechanics or thermodynamics to nonhomogeneous systems is essentially equivalent to the problem faced by Ornstein and Zernike.

B. An Approximate Treatment

The problem of the density distribution in an inhomogeneous fluid is identical with the problem of the radial distribution function. To see this, consider the equation of motion of a particle at R_1 with mean velocity $\mathbf{u}_1$.

$$m \frac{\partial(\rho_1 \mathbf{u}_1)}{\partial t} + k_B T \nabla \rho_1 + \rho_1 \int \rho_3 g(1,3) \nabla_1 V(13) d\mathbf{R}_3 = \mathbf{F}_1 \rho_1 \quad (12)$$

We use the notation (1,3) to indicate the argument of a function which depends on $\mathbf{R}_1$ and $\mathbf{R}_3$ separately, and the notation (13) to indicate the argument of a function which depends only on the relative separation $\mathbf{R}_3 - \mathbf{R}_1$. $\mathbf{F}_1$ is the external force acting on a

molecule at point 1. With one reservation, Eq. (12) is exact for any force $\mathbf{F}_1$,⁵³ in particular it will be exact for a force which is due to a molecule being fixed at the origin. On the other hand, the approximations necessary to bring Eq. (12) into a soluble form may then be unsuitable if molecule 1 is close to the origin. Certainly, the approximations which are to be made here, no matter what questions may arise about their validity in general, are suitable only if the density ρ_1 varies slowly from point to point, and therefore the approximations are really not suitable for determining the radial distribution function at small values of its argument. The reservation regarding the exactness of Eq. (12) concerns the treatment of velocity. The temperature is assumed constant and a Boltzmann distribution of velocities about $\mathbf{u}_1$ is assumed. The unknown function in Eq. (12) is $G(1,3)$. If the singlet density is constant, G reduces to $G(13)$, and may be presumed known. If a molecule is located at the origin, G becomes the triplet correlation function. Whatever the cause of the density variation, if ρ does not vary much over the distance R_{13} it is a very plausible first approximation to suppose that G is just the equilibrium radial distribution function, but evaluated at the density of the mid-point between 1 and 3. The subsequent analysis is elementary,³³ and gives the result

$$m \frac{\partial(\rho_1 \mathbf{u}_1)}{\partial t} + \nabla_1 \left\{ P_1 - \left[\frac{\rho}{30} \int R^3 V' \left(g + \left(\frac{\rho}{8} \right) \frac{\partial g}{\partial \rho} \right) d\mathbf{R} \right] \nabla^2 \rho_1 + \dots \right\} = \mathbf{F}_1 \rho_1 \quad (13)$$

where

$$P_1 = \rho_1 kT - (\rho_1^2/6) \int R V' g d\mathbf{R} \quad (14)$$

is the pressure at point 1. Higher order derivatives of ρ_1 and powers of lower order derivatives have been neglected. Except in certain circumstances, such as boundary layers, it suffices to keep only P_1 in a macroscopic equation of motion. In the molecular problem, where $\mathbf{F}_1$ represents the force due to a molecule at the origin, there is no question of P_1 sufficing. Rather the question is: does the series in Eq. (13) converge at all, and if it does, does it converge sufficiently rapidly for it to be adequate to keep only the first two terms in the series for interesting values

of $\nabla\rho_1$? Perhaps the most fundamental question is whether $G(1,3)$ is actually completely determined by the specification of the singlet density ρ in the finite region where $V(13)$ is non-vanishing. It is clear that the force $\mathbf{F}$ must determine uniquely both ρ and G , but it is still an assumption to proceed on the basis that the function ρ determines G uniquely. It seems probable to this author, if not certain, that the assumption is incorrect. The reason for this belief is the probable fact that P_1 cannot be identified with the macroscopic pressure. The discrepancy can be most easily examined for the two-dimensional-lattice gas, which will be treated shortly, but the problem briefly is that the dependence of P_1 on temperature which must be assumed in order to obtain the correct range of correlation for $T > T_c$ is not the same dependence which is indicated from the compressibility as determined by numerical extrapolations into the critical regions of high-temperature series.

Equation (13) is not quite identical with the consequences of the superposition approximation (33). The superposition approximation would give Eq. (13) if $\partial g(r)/\partial\rho$ were everywhere set equal to 0, both where it occurs explicitly in Eq. (13) and in

$$\nabla_1 P_1 = \left(\frac{\partial P_1}{\partial \rho_1} \right)_T \nabla \rho_1 \quad (15)$$

Without either prejudice or favor toward the applicability of Eq. (13) to critical phenomena, this discrepancy certainly indicates the inexactness of the superposition approximation, for P_1 must certainly be the macroscopic pressure if density correlations are short ranged. The superposition approximation is easily modified using the same physical arguments as went into Eq. (13), and the inconsistency is then removed.

Suppose that the singlet density, at all points within the region of interest, is close to a mean density ρ . Then, as in Eq. (1),

$$P_1 = \sum_0^{\infty} \left(\frac{\partial^n P}{\partial \rho^n} \right) \frac{(\rho_1 - \rho)^n}{n!} \quad (16)$$

Let

$$\delta_1 = \rho_1 - \rho \quad (17)$$

and for the present suppose that only linear terms in δ need be retained in Eq. (13), although later this restriction will have to be relaxed. Then

$$m \frac{\partial \mathbf{u}}{\partial t} + \rho^{-1} \frac{\partial P}{\partial \rho} \nabla \{\delta - \kappa^{-2} \nabla^2 \delta\} = \mathbf{F} \quad (18)$$

where

$$\kappa^2 = \frac{\partial P}{\partial \rho} \left\{ \frac{\rho}{30} \int R^3 V' \left[g + \left(\frac{\rho}{8} \right) \frac{\partial g}{\partial \rho} \right] d\mathbf{R} \right\}^{-1} \quad (19)$$

The denominator in this expression for κ^2 has the dimensions of energy times the square of length, and may be expected to have a magnitude of about kTl^2 , where l is a few Å. One expects this kind of magnitude because at the critical point

$$(\partial P / \partial \rho)_T = 0 = kT - (\rho/3) \int R V' [g + \frac{1}{2} \rho \partial g / \partial \rho] dR \quad (20)$$

The relation between Eq. (18) and the modification of the free energy which was previously discussed may be obtained most simply by taking a system in equilibrium in the absence of an external force. Ordinarily, these conditions imply constant pressure, and therefore constant density, but Eq. (18) evidently only indicates

$$\kappa^2 \delta - \nabla^2 \delta = 0 \quad (21)$$

(The constant of integration has been absorbed into δ .) If the free-energy density f which is usually ascribed to a density fluctuation is used

$$f = \frac{1}{2} \rho^{-1} \frac{\partial P}{\partial \rho} \delta^2 \quad (22)$$

minimization of the total free energy with respect to δ gives $\delta = 0$. If instead the free-energy density is taken to be

$$f = \frac{1}{2} \rho^{-1} \left(\frac{\partial P}{\partial \rho} \right)_T [\delta^2 + \kappa^{-2} |\nabla \delta|^2] \quad (23)$$

the equation of motion can be obtained by minimization of $\int f d\mathbf{r}$, and Eq. (21) is the immediate result. If $\mathbf{F}$ is the force due to a molecule fixed at the origin, the excess density δ will equal $\rho G(r)$, as follows from the definition of G . Then G satisfies

$$\kappa^2 G - \nabla^2 G = V(r) \sim 0 \quad (24)$$

where $V(r)$ is a short-ranged function, but is not identical to the intermolecular potential. The inadequacy of the approximations for small r makes the detailed behavior of $V(r)$ irrelevant; only the behavior of G at large r , that is at distances much greater than the range of interaction of the intermolecular potential, can be estimated with any hope of success. Equation (24) gives, in three dimensions,

$$G_3(r) \sim r^{-1} e^{-\kappa r} \quad (25)$$

This is, of course, the result of Ornstein-Zernike. Hart⁴⁵ has also given a thermodynamic derivation of this correlation function.

A closer examination of the nonlinear terms in δ in Eq. (13) indicates that they are not always negligible.³⁸ If the additional terms in Eq. (16) are retained, then the required modification of Eq. (18) is readily obtained; in equilibrium

$$\rho^{-1} \nabla \left[\sum_{n=1}^{\infty} \frac{\delta^n}{n!} \left(\frac{\partial^n P}{\partial \rho^n} \right) - \kappa^{-2} \left(\frac{\partial P}{\partial \rho} \right) \nabla^2 \delta \right] = \mathbf{F} \quad (26)$$

or, with

$$\begin{aligned} b^2 &\equiv \kappa^{-2} \rho (\partial P / \partial \rho) \\ \delta &= \rho G \end{aligned} \quad (27)$$

G satisfies

$$\kappa^2 G - \nabla^2 G + b^{-2} \sum_{n=2}^{\infty} \frac{\rho^n}{n!} \left(\frac{\partial^n P}{\partial \rho^n} \right) G^n = V(r) \sim 0 \quad (28)$$

where $V(r)$ is again a short-ranged potential. Evidently, the predicted behavior of G in the critical region depends crucially upon the curvature of the isotherms, as measured by the magnitude of the pressure derivatives in Eq. (28), and particularly on the number of these derivatives which vanish at the critical point. In the classical theory of the van der Waals gas,¹⁰⁸ the lowest nonvanishing derivative of the pressure at the critical point is the third. Voronel'¹³² has recently claimed that several methods actually indicated a positive value of the third derivative at the

critical point. These methods included direct *PVT* measurements, a second method based on the interpretation of the width of the flat top of the coexistence curve when measurements are made in long vertical tubes, a third method based on the apparent discontinuity in the constant volume heat capacity during the transition from the one-phase to the two-phase system at the critical point, and finally a calculation of relative values based on a law of corresponding states. Reasonable agreement between the different estimates was obtained for a wide variety of compounds. Still, as was discussed in an earlier section, the weight of evidence is that a careful determination of the coexistence curve in short tubes will give a cubic coexistence curve, and this conclusion is buttressed by numerical extrapolations in the theory of the Ising lattice.^{6,24} Certainly it does not follow from the inadequacy of the van der Waals type equation that the third derivative *must* vanish, but it seems likely, and this feeling is encouraged by many careful *PVT* measurements.^{108,136} Zimm¹⁴¹ has conjectured on the basis of the superposition approximation that all derivatives vanish at the critical point. While the question of the number of vanishing derivatives must remain unanswered, it is still useful and interesting to see what modifications must be made in the linear theory for an assigned number of vanishing derivatives.³⁸

In two dimensions Eq. (24) has the solution

$$G_2 \sim K_0(\kappa r) \quad (29)$$

where $K_0(Z)$ is the Hankel function of imaginary argument:

$$\begin{aligned} K_0(Z) &\rightarrow (\pi/2Z)^{\frac{1}{2}} e^{-Z} & \text{for } Z \gg 1 \\ K_0(Z) &\rightarrow -\ln Z & \text{for } Z \ll 1 \end{aligned} \quad (30)$$

The behavior of G_2 at large distances is physically reasonable; at small distances, on the other hand, Eq. (30) indicates a logarithmic divergence. The infinity at the origin is not in itself cause for alarm, for the original equations are known to be inadequate at small r . The problem here is that the scale of r as determined by κ and Eq. (30) indicates that for any r the correlation will become infinite as κ vanishes, that is at the critical point. Certainly Eq. (28) rather than (24) must be used for two-dimensional

systems. Although it is not known how many pressure derivatives vanish even for the two-dimensional system, where many other exact results are known, it is perhaps better to couple the known results on the coexistence curve to the classical relation between the pressure derivatives and the shape of the coexistence curve, than to have no hypothesis at all. In the classical theory $(\partial P/\partial \rho) \propto (T - T_c)$ if $\rho = \rho_c$, and is negative if T is less than T_c . If the m th derivative of the pressure is the lowest nonvanishing one at the critical point, the coexistence curve has the shape

$$T_c - T \propto (\rho^l - \rho_c)^{m-1} \quad (31)$$

where ρ^l is the density at the liquid end of the tie line. Since the two-dimensional-lattice gas has a coexistence curve given by Eq. (31) with $m = 9$,⁶⁹ this coupling of thermodynamic and statistical-mechanical methods gives, from Eq. (28),

$$\begin{aligned} -\nabla^2 G + \beta_m G^m &= V(r) \sim 0 \\ \beta_m &\equiv b^{-2} m!^{-1} \rho_c^m (\partial^m P / \partial \rho^m)_c \end{aligned} \quad (32)$$

at the critical point, with $m = 9$. The actual value of m may be left as arbitrary for a few steps. A detailed analysis of Eq. (32)³⁸ shows that the only solution which is asymptotically 0 is

$$\begin{aligned} G_2 &= ar^{-k} \\ k &= 2(m-1)^{-1} \\ a^{m-1} &= 4[(m-1)^2 \beta_m]^{-1} \end{aligned} \quad (33)$$

With $m = 9$, $k = \frac{1}{4}$. This is a particularly interesting prediction in view of the derivation by Kaufman and Onsager⁵⁶ that G_2 is, exactly, asymptotically proportional to $r^{-\frac{1}{4}}$ at the critical point. Moreover, the value of a can be approximately determined³⁸ with Debye's procedure²³ for the estimation of κ^2

$$\kappa^2 = 4(T - T_c)(l^2 T_c)^{-1} \quad (34)$$

for two dimensions, where l is a short-ranged interaction length which must be set equal to unity for a square lattice. This gives $a = 0.7268$ (incorrectly given as 0.86 in Reference 38), as compared with the Kaufman-Onsager value of $a = 0.7786$. It should be pointed out that the Kaufman-Onsager value of a is an approximation derived for correlations along a row. They have an exact

result for correlations along a diagonal, and the author is indebted to Professor M. E. Fisher for pointing out that this exact result may be interpreted to indicate that $a = 0.7034$. The agreement seems more than accidental, and is strong support for the conjecture $m = 9$. Yet the classical procedure by which this value of m was deduced from the shape of the coexistence curve is certainly suspect, although there is really no statistical-mechanical evidence against it. The reason for this lack of evidence is that the classical procedure requires an estimate of $(\partial P/\partial \rho)$ for T less than T_c , long-range order or phase separation being excluded, and statistical mechanics thus far is incapable of giving an exact description of this region of metastable and unstable states. There is no question that the expression used for the compressibility is inexact both for the macroscopic compressibility and for an estimate of κ^2 at temperatures greater than T_c . The series extrapolation methods strongly indicate that the reciprocal compressibility is proportional to $(T - T_c)^{1/6}$,²⁵ rather than being a continuation of the first-power dependency under the coexistence curve, and also, Onsager's calculation⁹⁰ of the mean range of correlation in the critical region requires that κ rather than κ^2 be proportional to $T - T_c$. Onsager's result could, of course, be entered in Eq. (28) to calculate $G_2(r)$ for $T > T_c$.

The situation in three dimensions is somewhat more complicated. Although solutions of the form given in Eq. (33) also exist for G_3 , they are not the solutions which converge most rapidly to 0 in three dimensions, and consequently do not minimize the free energy. The free energy required to form the equilibrium distribution of density around a fixed molecule, at the critical point, is proportional to

$$\int \left\{ \frac{1}{2} |\nabla G_3|^2 + \beta_m (m + 1)^{-1} G_3^{m+1} \right\} r^2 dr \quad (35)$$

The stationary value of this integral results from the function G_3 which satisfies Eq. (32). But a minimum value of the free energy in three dimensions is not obtained for a function of the form (33), but rather for a function which is asymptotically proportional to r^{-1} . This will be true whenever $m > 3$. If the thermodynamic significance of the terms in Eq. (32) is to be preserved, m must be odd, and the only exception to the previous statement comes for

$m = 3$. For this value a closer analysis is required,³⁸ and it is found that the proper solution of Eq. (32) is

$$G_3 \sim r^{-1}(\ln r)^{-\frac{1}{2}} \quad (36)$$

Levanyuk⁷² has considered a problem identical in substance to the introduction of nonlinear terms in Eq. (24). He examined the theory of light scattering at order-disorder transition points according to the formalism of Landau and Lifshitz.⁶⁵ In that formalism β_3 does not vanish, and he concluded that the Ornstein-Zernike theory is inadequate at temperatures sufficiently close to T_c . This, of course, is what has been found here, *if* $m = 3$. An actual prediction in this case would require numerical solutions of Eq. (28).

Fisher^{30,31} has used the results of series extrapolations for the susceptibility to deduce a considerably different $G_3(r)$. From the assumption that $\kappa^2 \propto (T - T_c)^2$ in three dimensions, a relation known to hold in two dimensions, he concludes that $G_3(r) \sim r^{-4}$ at the critical point.

A very interesting paper by Yvon¹³⁷ should be mentioned. Yvon treats the perturbation of a fluid system under the influence of a potential field of small magnitude. The variation in singlet density can be obtained in terms of the potential energy perturbation, and also in terms of the radial distribution function. A second relation between the perturbing potential and the perturbed singlet density is derived on the basis of a cluster expansion of the activity. From these two equations a cluster expansion of the radial distribution function is obtained which is very close to and probably identical with that derived by Rushbrooke and Scoins.^{109a} It can be ascertained that the Ornstein-Zernike expression for $G(r)$ is obtained in the critical region. κ^2 is shown to be proportional to $\partial P / \partial \rho$, but the proportionality constant is known only in the form of a cluster expansion. His relations are worth writing down here

$$G_3(r) = (4\pi L_2 \rho)^{-1} r^{-1} \exp \left\{ -r \left[\left(\frac{\partial P}{\partial \rho} \right)_T (k_B T L_2)^{-1} \right]^{\frac{1}{2}} \right\} \quad (37)$$

$$L_2 = \frac{1}{6} \int K_{12} r^2 4\pi r^2 dr \quad (38)$$

$$K_{12} = \rho f_{12} + \rho^2 f_{12} \int f_{13} f_{23} d\tau_3 + \dots \quad (39)$$

$$f_{12} \equiv \exp [-V(r_{12})/k_B T] - 1 \quad (40)$$

It is easily seen that this set of equations is in agreement with Eq. (19) in the limit of low densities, where only the first term in Eq. (39) is retained. But, of course, the equations are of interest only in the critical region. One remark on Eq. (39) should be made; the virial expansion of K_{12} is quite different from the virial expansion of $G(r)$, and K_{12} probably converges to zero more quickly than $G(r)$. However, f_{12} does not appear in every term of the expansion and it is not certain that the second moment of K_{12} is finite at the critical point, which is a necessary condition for the validity of the Ornstein-Zernike theory.

C. Summation Methods

Recently many workers have independently arrived at a rearrangement of cluster sums which offers considerable hope for the numerical evaluation of the radial distribution function.^{43,50,70,77,78,81,82,109} A concise and clear review of this accomplishment has been given by Mazo.⁷⁵

Unfortunately, even after all possible simplifications have been made, there remains in these equations for $g(r)$ an infinite series of cluster integrals in $g(r)$. If this series of so-called "elementary" diagrams is neglected, a closed pair of integral equations results which can be solved for $g(r)$. The general exact result has the form

$$G(r_{12}) = X(r_{12}) + \rho \int X(r_{13}) G(r_{23}) d\mathbf{r}_3 \quad (41)$$

This is, of course, the form of the Ornstein-Zernike integral equation, Eq. (7), as has been stressed particularly by Meeron.^{77,78} But whether this resemblance is one of form or substance depends entirely on the nature of $X(r)$. In the Ornstein-Zernike equation, X is assumed to be a short-ranged function; that is, it becomes negligibly small as r increases beyond the range of the intermolecular potential. However, the approximate cluster summation technique gives an X that is long-ranged, as Green pointed out.⁴³ In the approximation which neglects elementary diagrams,

$$\begin{aligned} G(r) &\sim r^{-2} \\ X(r) &\sim r^{-4} \end{aligned} \quad (42)$$

For Eq. (1) to yield the Ornstein-Zernike equation, it is necessary that $\int r^2 X(r) d\mathbf{r}$ be finite, contrary to Eq. (42). Green also showed that the results of Eq. (42) invalidate, at least in part, the approximation used in its derivation, that is, the neglect of elementary diagrams. Additional evidence that X is not short-ranged was given by Stillinger and Frisch.¹²³ They showed that neglect of elementary diagrams in the treatment of a two-dimensional-lattice gas gave

$$G_2(r) \sim r^{-\frac{1}{2}} \quad (43)$$

in contrast to the result already given for the Ornstein-Zernike equation, and also in contrast to the exact $r^{-\frac{1}{2}}$ behavior. They also found that the neglect of elementary diagrams was invalidated by the results obtained. The neglect of elementary diagrams is sometimes called the hypernetted chain approximation.

Rushbrooke¹⁰⁹ has shown that the hypernetted chain approximation, when linearized, gives just the Born-Green-Kirkwood linearized equation. However, Katsura and Harumi,⁵⁵ in their discussion of the singularities of the linearized B-G-K equation, have pointed out a resemblance between it and the hypernetted chain approximation even when the latter is not linearized. The pressure-volume isotherms of both equations have an infinite number of singularities at temperatures below the critical temperature, and consequently cannot be reliably extended into the liquid region. It should be noted that Katsura's calculation was based on a strictly linearized equation, whereas some of the earlier work involved the replacement of functions of r in certain regions by constants which were not necessarily the same constants as in a strictly linearized theory. In spite of its unfortunate behavior below the critical temperature, the linearized B-G-K equation and also the hypernetted chain equation should not be too hastily regarded as nonsensical in the critical region. Sundheim and Rubin¹²⁵ have compared the predicted critical constants of the linearized and nonlinearized B-G-K equations; they found excellent agreement between the two equations for the critical volume and critical temperature, much closer to each other than to experiment. Of course, the shape of the coexistence curve and the behavior of isotherms in the critical region form a much more delicate test of a theory than do the values of the critical constants.

The work of Brout on the three-dimensional Ising lattice^{13,14} is one of the more interesting applications of diagram summation techniques to statistical mechanics. In Brout's theory diagrams are classified according to the power of $1/Z$ to which they contribute. Z is the number of neighbors with which any one spin interacts, and since the thermodynamic quantities are evaluated only to the power $1/Z$ the theory may be said to describe the high-density behavior of the Ising lattice. There is, of course, no reason to be confident that the predictions of the theory will be accurate in the critical region, because an approach to the critical point is effected with constant Z . Brout first approximated the high-density behavior with a summation of ring diagrams,¹³ but found that this procedure led to different temperatures for the singularities in the heat capacity and in the magnetic susceptibility, and also to a violation of a sum rule which expressed the condition of constant number of spins. He then found that imposition of this sum rule gave the same temperature for the two singularities, and that the content of his theory was identical with that of the spherical model for temperatures greater than T_c , and was an improved generalization of the spherical model for lower temperatures (however, see Reference 51, p. 1777). In his second paper,¹⁴ he supplied the previously neglected diagrams and showed that his theory was an exact one to order $1/Z$. In both the original and revised theories the correlation between spins had exactly the form of the Ornstein-Zernike relation and the susceptibility was proportional to $(T - T_c)^{-1}$. However, the behavior of the heat capacity in the critical region changed drastically between the two theories; in the ring diagram summation the heat capacity went to infinity at the critical point as $(T - T_c)^{-\frac{1}{2}}$, while in his revised theory the heat capacity was finite at the critical point although its derivative became infinite as $(T - T_c)^{-\frac{1}{2}}$.

IV. LIGHT SCATTERING AND X-RAY DIFFRACTION

At the moment of writing, experimental verification of the Ornstein-Zernike radial distribution function is lacking. Several experimental investigations are underway, but the extremely difficult nature of experimental measurements in the critical

region makes it improbable that a final conclusion will soon be reached. It is clear that light scattering and small angle X-ray scattering are the least ambiguous methods for the determination of the radial distribution function, since the angular distribution of scattered intensity is proportional to the Fourier transform of the radial distribution function in the critical region. There are, of course, technical difficulties connected with the conversion of this transform, but the main interest is in the asymptotic behavior of $g(r)$ and many of the usual problems are irrelevant. The experimental situation is considerably worse than one might expect. The bulk of experiments known to this author may be divided into two classes; those experiments which show substantial agreement with the Ornstein-Zernike predictions, and those which show clear disagreement. There are relatively few doubtful experiments. One of the major sources of difficulty is that the total scattered intensity of light becomes very large, and not just the angular dissymmetry. The consequently large amount of multiple scattering makes the dissymmetry measurements difficult to interpret close to the critical point, while farther away from the critical point the dissymmetry has become small. The X-ray work is not troubled by multiple scattering, but there are difficulties in working at the extremely small angles which are relevant for T near T_c .

M. S. Green has informed the author of his intention to review the scattering experiments for the next issue of this series; by that time the experimental situation may be much clearer than it is now. However, it should be useful briefly to trace the development of the theory and to refer to a few of the experimental papers which point up the conflicts in the literature.

In the Einstein-Smoluchowski theory²⁷ the scattering system is divided into cells whose greatest dimension is much smaller than the wavelength of the scattered light. The fluctuation in density or composition in one of these cells is assumed to be independent of the fluctuations in any of the other cells, and the scattered light has an intensity proportional to the square of the refractive index fluctuation in the cell. With two exceptions, these assumptions are quite good. The first exception occurs when the molecules of the system have dimensions which are not much smaller than the wavelength, for example, if the molecules are high polymers.

The second exception occurs in the critical region, as was first noticed by Ornstein and Zernike.⁹²⁻⁹⁴ For many years after Einstein's work there were doubts about the validity of defining a local refractive index; the doubt was essentially whether the local field acting on a molecule, as distinct from the external electromagnetic field, arose solely in the distribution of polarizability in the immediate environment of the molecule, or whether the local field also received contributions from the surface polarization on the boundary of the system. The former alternative turns out to be correct,³² and a local refractive index can be defined which is, to a very good first approximation, a function only of the local density. In the critical region there are small corrections to the refractive index theory which arise because of the great range of $g(r)$, but the corrections are quite negligible. Because the index of refraction is virtually unity for X-rays, the problem of the local field does not arise in X-ray scattering.

With k the wave number of the light in the medium, $\mathbf{e}_i$ the direction of propagation of the incident wave, and $\mathbf{e}_s$ the direction of the scattered wave, the scattered amplitude is proportional to

$$\int \Delta n(R) \exp [ik(\mathbf{e}_i - \mathbf{e}_s) \cdot \mathbf{R}] d\mathbf{R} \quad (44)$$

where Δn is the fluctuation in refractive index. For a one-component system Δn is proportional to the fluctuation in local number density, that is

$$\Delta n \propto \sum \delta(\mathbf{R} - \mathbf{R}_i) - \rho \quad (45)$$

and

$$I \propto 1 + \rho \int G(r) \frac{\sin wr}{wr} d\mathbf{r} \quad (46)$$

$$w \equiv 2k \sin (\theta/2)$$

where θ is the angle of scattering and the incident light is taken to be polarized. The same formula, Eq. (46), holds for X-ray scattering. A Fourier inversion of the scattering envelope is possible in principle, but a more direct test of a suggested $G(r)$ is simply to use the above formula. For example, $G(r) = ar^{-1} \exp(-\kappa r)$ gives

$$I \propto 1 + 4\pi\rho a/(\kappa^2 + w^2) \quad (47)$$

The first term on the right-hand side is small in the critical region and a graph of the reciprocal intensity against w^2 should be a straight line. Alternatively, the intensity can be graphed against $w^2\kappa^{-2}$ and the initial slope measured; the slope should increase as the critical point is approached and should be inversely proportional to the temperature difference from the critical point.

Both X-ray and light scattering sometimes show very good agreement with the predictions of the Ornstein-Zernike theory,^{10,100,140} and sometimes remarkable discrepancies.^{11,100} Some of the discrepancies¹⁰⁰ are easily, perhaps too easily, ascribed to multiple scattering, particularly when the two components of a mixture in the critical mixing region have very different refractive indices. Some of the discrepancies¹¹ seem completely mysterious. As yet, there is no better theoretically based equation to test than the Ornstein-Zernike equation, but Frisch and Brady^{41a} have taken an interesting speculative step toward obtaining one. They consider a $G(r)$ which behaves like $r^{-1} \exp(-\kappa r)$ for $\kappa r \gg 1$, and like $r^{-\frac{5}{2}}$ for $\kappa r \ll 1$ (Fisher's suggestion), and exhibit a comparison with X-ray diffraction data. The fit appears to be as good as given by the Ornstein-Zernike equation, but the data are insufficient to verify an improvement.

As was mentioned earlier, Levanyuk has pointed out a possible inaccuracy in the Ornstein-Zernike theory of light scattering in the critical region, but his corrections were not carried to the numerical stage. His equations were essentially only a possible example of a nonlinear equation for $G(r)$, which has already been considered here.

There are many experimental investigations of X-ray and light scattering in the critical region which we have not attempted to review.

V. VISCOSITY

A few general remarks on philosophy will set the tone for the detailed calculations that follow. The most important remark is that the calculations made here do not rest directly on a general formal theory of transport processes or, in the calculation of heat capacity, even on the simpler formalism of equilibrium statistical mechanics. With one exception the exact use of the radial

distribution function to compute equilibrium or transport properties requires the distribution function only at small values of its argument, the reason being that $g(r)$ is multiplied by the intermolecular potential or some derivative of it in the integrals which give the properties.^{48,53} Even in the exception, the calculation of the compressibility in the critical region, the use of the long-ranged behavior of $g(r)$ is permissive rather than mandatory. Either of

$$P = \rho kT - \frac{\rho^2}{6} \int r V'(r) g(r) d\mathbf{r} \quad (48)$$

$$\left(\frac{\partial P}{\partial \rho} \right)_T = \frac{kT}{1 + \rho \int G(r) d\mathbf{r}} \quad (49)$$

can be used to calculate the compressibility, the first equation involving the short-range behavior of g and the second involving the long-range behavior of g , at least in the critical region. Equation (49) originates from fluctuation theory, and results essentially from the observation that the work required to produce a number fluctuation in a macroscopic domain is proportional to the reciprocal compressibility. This attention to fluctuations, and particularly to the long-wavelength components where an application of intuition can be risked, is the basis of the detailed calculations that follow. The calculations are not developed formally and are by no means rigorous. It is probable that exact relations between fluctuations and the long-ranged behavior of distribution functions can be developed formally, as for instance in the fluctuation expression for the heat capacity. But these are also likely to involve higher order distribution functions than the second, as in the expression for the heat capacity.

Consider now a binary mixture in the critical region subjected to simple shear flow between parallel plates. There will be large-scale composition fluctuations and these will vary from one time to another, or from one member of an ensemble of similar systems to another member. The dynamical behavior of a particular member of this ensemble is quite complicated, even though the behavior will be described by macroscopic equations of motion and diffusion. An examination of many effects which turn out to be

small has been given, but a repetition seems unnecessary and only the major cause of the anomalous viscosity will be treated here.³⁵ This cause turns out to be the frictional dissipation of energy which occurs when the sheer flow interacts with the spontaneous composition fluctuations. The course of analysis involves first a description of the diffusion in the space of the singlet distribution function, from this is derived a formal expression for the entropy production, which becomes an integral over the perturbed pair distribution function, and finally the perturbation of $g(r)$ induced by the imposed velocity gradient is determined. The proportionality constant between the entropy production and the square of the velocity gradient is the increment in viscosity caused by the critical fluctuations.

In the barycentric frame, let $\mathbf{i}$ be the diffusion flux in mass per square centimeter per second of component 2. In this frame the net transport of mass is zero. Let c be the mass fraction of component 2, that is the mass of 2 in a unit mass of the mixture, and let ν be the total mass density. Then

$$\nu \frac{dc}{dt} = \nu \left(\frac{\partial c}{\partial t} + \mathbf{v} \cdot \nabla c \right) = -\nabla \cdot \mathbf{i} \quad (50)$$

$$\mathbf{i} = -\alpha \nabla \mu \quad (51)$$

$$\mu = (\mu_2/m_2) - (\mu_1/m_1) \quad (52)$$

Subscripts will be used for components whenever any ambiguity might arise. In Eq. (50) $\mathbf{v}$ is the center of mass velocity and in Eq. (51) α is a diffusion constant and μ a chemical potential; μ_i and m_i are the chemical potentials and mass, per molecule, of component i . Except for the generalization to the critical region, the presentation of the equations of motion follows that given by Landau and Lifshitz.⁶⁶ Accompanying the flux $\mathbf{i}$ is an entropy production $\dot{s}$ given by

$$T\dot{s} = - \int_V \langle \mathbf{i} \cdot \nabla \mu \rangle d\mathbf{R} \quad (53)$$

where the integral extends over the total domain of the mixture, or any large part of volume V . Although this equation is standard, its application here requires some explanation. In the conventional use of Eq. (53), a product of the separate averages of

flux and force is used in the integrand, while here an average of the product is used. It is evident that the present equation would indicate an entropy production in any system observed to be in a state of fluctuation, even in the absence of external forces. This is intuitively quite reasonable, for ordinarily the entropy is a property of the complete ensemble, but in a subset of the ensemble the system is confined to a smaller volume of phase space and this increased localization should show up as a lowered entropy. After an observation, this subset of phase points will diffuse throughout phase space and eventually reach an equilibrium distribution in it. A certain amount of entropy will be introduced during this evolution. But this is a transient production of entropy, while what is being calculated is the steady-state production, which has its ultimate origin in the transfer of energy at the surface of the fluid. Equations (51) and (53) give

$$T\dot{s} = \alpha \int \langle \nabla \mu \cdot \nabla \mu \rangle d\mathbf{R} \quad (54)$$

$$= -\alpha \int \langle \delta \mu \nabla^2 \mu \rangle d\mathbf{R} \quad (55)$$

where $\delta \mu$ is the fluctuation in chemical potential. The relation between μ and n , the number concentration of one of the species, say 2, must be generalized in the critical region just as was the relation between pressure and density in the one-component system. Debye's work²³ gives a possible way of obtaining this generalization from a molecular theory. One has

$$\delta \mu = \left(\frac{\partial \mu}{\partial n} \right)_{P,T} [\delta n - \kappa^{-2} \nabla^2 (\delta n)] \quad (56)$$

where δn is the fluctuation in n . A Fourier resolution of δn

$$\delta n = \int n_k e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} \quad (57)$$

gives

$$\delta \mu = \kappa^{-2} \left(\frac{\partial \mu}{\partial n} \right)_{P,T} \int (\kappa^2 + k^2) n_k e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} \quad (58)$$

Now it is well-known, and easily shown, that

$$\langle n_k n_{k'} \rangle = \delta(\mathbf{k} + \mathbf{k}') [(2\pi)^{-3} n + n^2 G_k] \quad (59)$$

$$G_k \equiv (2\pi)^{-3} \int G(r) e^{-i\mathbf{k} \cdot \mathbf{r}} d\mathbf{r} \quad (60)$$

where $G(r) = g(r) - 1$ is the radial distribution function of component 2 in the mixture, less its asymptotic value of unity. G_k is very large for the long-wavelength fluctuations under consideration; G_0 is, of course, infinite at the critical point. The constant term in the brackets of Eq. (59) may consequently be suppressed. Equations (55) and (58) then give

$$\frac{T\dot{s}}{V} = \alpha n^2 \left[\kappa^{-2} \left(\frac{\partial \mu}{\partial n} \right)_{P,T} \right]^2 \int k^2 (k^2 + \kappa^2)^2 G_k d\mathbf{k} \quad (61)$$

The integral over k should be understood to have a cutoff at some upper wave number $k_{\max}$, since the macroscopic equations used require, equivalently, some partial averaging of point functions over small elements of volume or a suppression of rapid spatial variations through the cutoff. It may also be observed that the appearance of only one radial distribution function in the equation—instead of the three possible for a binary mixture—results from the implicit assumption of constant pressure; concentration fluctuations of 1 and 2 are then proportional (see also Pearson⁹⁶).

Now the rate of entropy production in the absence of critical fluctuations is given by^{35,66}

$$T\dot{s}/V = \eta^0 d^2 \quad (62)$$

where η^0 is the viscosity in the absence of critical fluctuations and must be obtained from the actual data by interpolation, while d is the velocity gradient. The increment in viscosity due to critical fluctuations must have the same form, and accordingly the perturbation in $G(r)$ must be obtained to the second order in d . It is assumed that diffusion in pair space follows the same equations as diffusion in singlet space, with the obvious necessary modification that the diffusion constant must be doubled, since the separation of two molecules may be altered by a jump of either of them. Equations (50) and (51) would give for the diffusion in singlet space the equations

$$v \frac{\partial c}{\partial n} \frac{dn}{dt} = \alpha \nabla^2 \mu \quad (63)$$

where μ is related to n through Eq. (56). The equation for G is

then obtained from Eq. (63) by replacing α by 2α , and n by G . The result is

$$\mathbf{v} \frac{\partial c}{\partial n} \frac{dG}{dt} = 2\alpha \left(\kappa^{-2} \frac{\partial \mu}{\partial n} \right) (\kappa^2 \nabla^2 G - \nabla^2 \nabla^2 G) \quad (64)$$

The interaction of G with the velocity field is concealed in the substantial time derivative of G . If the velocity is taken along the x direction and the velocity gradient along the z direction, one has $\mathbf{v} = \mathbf{e}_x z d$, where z and x are the components of $\mathbf{r}$.

$$\frac{dG}{dt} = \frac{\partial G}{\partial t} + \mathbf{v} \cdot \nabla G = dz \frac{\partial G(r)}{\partial x} \quad (65)$$

The partial time derivative of G vanishes because the goal of the calculation is the stationary-state entropy production. An iterative solution of Eq. (64) is perfectly feasible since d is the expansion parameter of the perturbation series and the function multiplying d in Eq. (65) can always be taken in the next lower order of approximation from that being solved for in Eq. (64). The iteration has actually been carried out to the fourth power of $d^{9,35}$; the second-order calculation gives the viscosity increment and the fourth-order perturbation gives the dependence of the viscosity on the velocity gradient. The zeroth approximation to G is, of course, the equilibrium function, of the form $G_0(r) = ar^{-1} \exp(-\kappa r)$.

The result of the calculation to second order is that η_M , the macroscopically observed viscosity, is given by

$$\eta_M = \eta^0 + (\rho n_2 \partial c_2 / \partial n_2)^2 (a/40\alpha) \kappa^{-1} \quad (66)$$

This is a rather simple equation and a partial test could readily be given, since the major dependence on temperature and composition resides in κ . For a mixture at the critical composition the viscosity increment is predicted to be proportional to $(T - T_c)^{-\frac{1}{2}}$. But in general one wants to know that the values of a , α , and l used in fitting the data are reasonable, and one also wants the composition dependence of κ . This requires some straightforward work which will be briefly summarized.

First, the diffusion constant of an equivalent ideal mixture can be introduced through

$$\frac{\mathbf{i}}{m_2} = -D_{id} \left(\frac{\partial \ln a_2}{\partial \ln x_2} \right)_{P,T} \nabla n_2 \quad (67)$$

where a_2 is the activity and x_2 the mole fraction of 2. D_{id} should not change much with composition and so can be compared with typical values of diffusion constants. Expressed as a friction constant

$$D_{id} = k_B T / m_2 \beta \quad (68)$$

and β should range from 10^{12} to 10^{14} reciprocal seconds. A thermodynamic expression for κ^{35} can be obtained from

$$\left(\frac{\partial \Pi}{\partial n_2} \right)_{\mu_1, T} = k_B T \left[1 + n_2 \int G(r) d\mathbf{r} \right]^{-1} \quad (69)$$

$$\cong -V_1^{-1} \left(\frac{\partial \mu_1}{\partial n_2} \right)_{P, T} \quad (69a)$$

where Π is the osmotic pressure and V_1 is the partial molecular volume of 1. With the Ornstein-Zernike $G(r)$ these equations give

$$\frac{4\pi a}{\kappa^2} = -\frac{V_1}{q_2} \left[\frac{k_B T}{(\partial \mu_1 / \partial q_2)_{P, T}} + \frac{V_2}{V_1} \right] \quad (70)$$

In principle, all parameters can now be determined. A combination of light-scattering angular-dissymmetry measurements and thermodynamic measurements will give κ and a , as will absolute light-scattering intensity measurements, and diffusion measurements will give D_{id} ; all the other quantities can be obtained from essentially routine measurements. In practice, the complete data exist for no system and approximate thermodynamic formulae are required. The Flory-Huggins equation (47) has been chosen as a compromise between simplicity and accuracy, and gives

$$(\partial \mu_1 / \partial q_2)_{P, T} = -k_B T [\varphi_1^{-1} - (1 - m^{-1}) - 2(\mu_0 / T) \varphi_2] \quad (71)$$

where $m = V_2 / V_1$ and μ_0 , an energy parameter taken to be independent of temperature and composition, can be obtained from the value of the critical temperature. An application of this

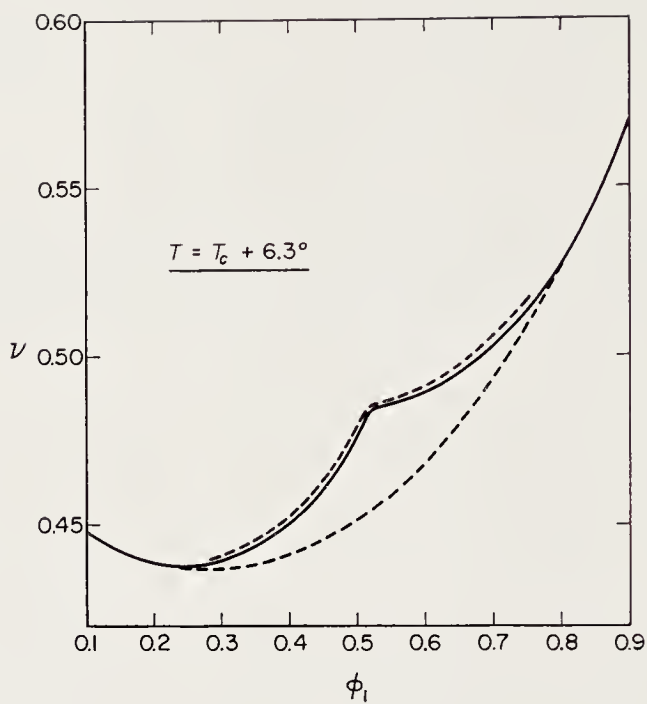


Fig. 2

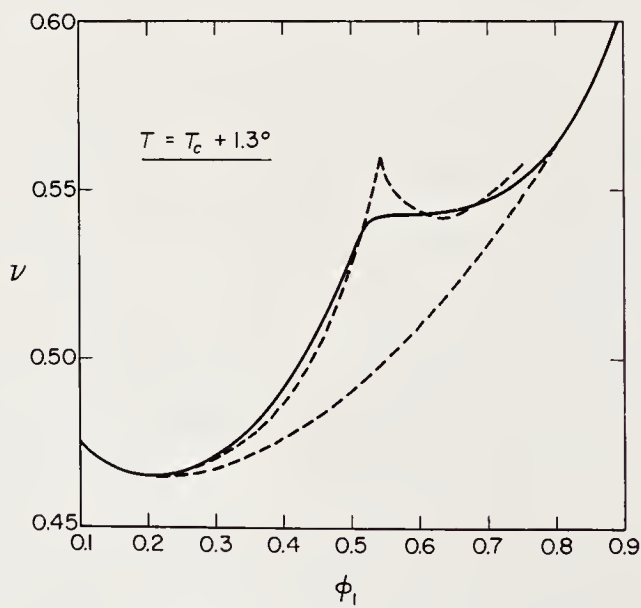


Fig. 3

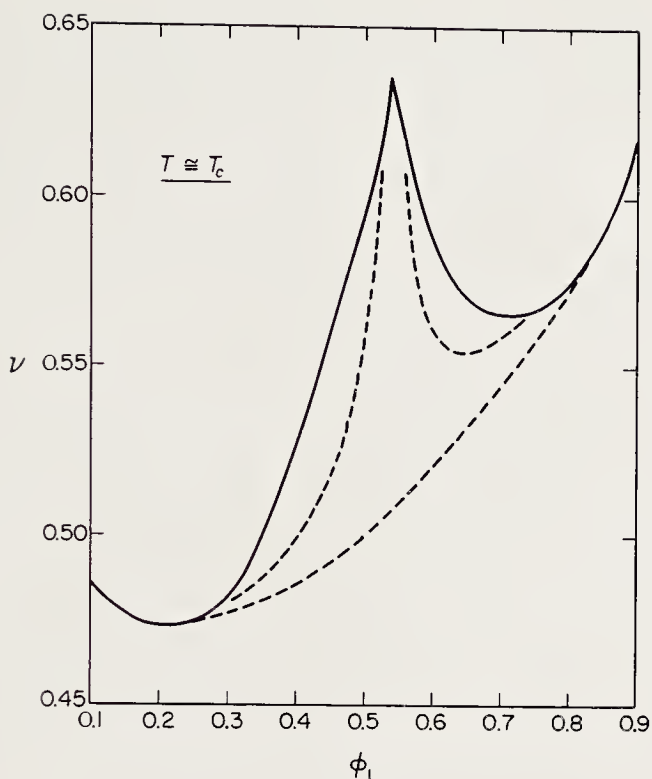


Fig. 4

Figs. 2, 3, 4. The viscosity in centistokes ν is plotted against the volume fraction ϕ_1 of $i\text{-C}_8\text{H}_{18}$ in the mixture C_7F_{16} , $i\text{-C}_8\text{H}_{18}$. The solid curve is experimental and the upper and lower dashed curves are, respectively, the theoretical ν and the estimated ν for a system without long-range composition correlations. (2) $T - T_c = 6.3^\circ$, (3) $T - T_c = 1.3^\circ$, (4) $T - T_c \cong 0^\circ$. [After Fixman, M., *J. Chem. Phys.* **36**, 310 (1962).]

equation to the temperature variation of κ along the critical composition can be used to relate a to Debye's l :

$$a = 3V_2(2\pi l^2)^{-1} \quad (72)$$

This completes the set of equations required to compare the theoretical and experimental viscosity increments as functions of temperature and composition. Figures 2, 3, and 4 give such a comparison for the system iso-octane-perfluoroheptane; the viscosity data are due to Reed and Taylor.¹⁰¹ The one unknown

parameter which must be estimated is the quantity $\beta a^{\frac{1}{2}}$, which was taken equal to $3.55 \times 10^{12} \text{ A}^{\frac{1}{2}} \text{ sec}^{-1}$. This is a reasonable value for the product since a should be of the order of 1 A, although perhaps the product is somewhat too large. If Brady's value of l is used (Reference 10, and personal communication), $l = 6 \text{ A}$, and Eq. (26) gives $a = 5 \text{ A}$, or $\beta = 1.6 \times 10^{12} \text{ sec}^{-1}$.

If the viscosity increment in Eq. (66) is denoted by $\Delta\eta^{(2)}$ the fourth-order perturbation calculation⁹ gives

$$\Delta\eta = \Delta\eta^{(2)} [1 - \text{const.} \times d^2 \kappa^{-4} + \dots] \quad (73)$$

The rather complex coefficient in Eq. (73) is given in Reference 9. It is evident that the series becomes divergent at the critical point, but in practice the coefficient in Eq. (73) is so small that it was estimated for the Reed and Taylor system that $T - T_c$ had to be about 0.2° or smaller for the dependence of the viscosity on the velocity gradient to be detectable. The effect is known to exist,^{95a} and is quite striking in magnitude, but because the only experiment was done in a capillary viscometer, where d varies across the capillary, a quantitative interpretation is difficult. An attempt is being made to develop $\Delta\eta$ as a function of d for large d (unpublished work by W. Botch and the author).

In retrospect it seems that the theory has been reasonably successful quantitatively, and not just in rough agreement with the experiment. Some encouragement for the belief that the agreement is not fortuitous can be gleaned from the consideration of a problem quite different on the surface: the problem of the viscosity of a dilute electrolyte solution. What makes this problem similar to that of the viscosity of a critical mixture is the occurrence in both systems of a long-ranged radial distribution function, the $g(r)$ of an electrolyte solution having the form of an Ornstein-Zernike correlation. The intermolecular potentials are vastly different in the two situations, being short-ranged for the critical mixture and long-ranged for the electrolyte solution. If the same technique for the calculation of a viscosity that has been developed here is applied to the electrolyte solution, the same viscosity is found as had been found earlier by more straightforward means.^{35,91} This concurrence may be taken to indicate that no gross errors have been made, but of course it cannot validate the application of macroscopic concepts to the local fluctuations in a critical mixture.

It should be noted that experimental interest in the viscosity of binary mixtures in the critical region has had a wide distribution in both space and time.^{41,95,101,106,117-120} The qualitative notion that the anomalous viscosity is somehow related to macroscopic inhomogeneities appeared in the earliest papers, the resemblance to the large velocity of colloidal solutions being inescapable. In the measurement of viscosity, as in the measurements of so many other phenomena in the critical region, a hysteresis was found only after the mixture had been taken to the critical point and phase separation occurred, and, more surprisingly, it was found that the hysteresis was greater for observations farther from the critical point than observations at the critical point. The occurrence of hysteresis can be understood in a general way, since the equilibration of $g(r)$ which is required when the mixture is raised from $T < T_c$ through $T > T_c$ must be slow because the diffusion constant vanishes at the critical point. But the details remain mysterious.

The problem of gas viscosities in the critical region will be briefly discussed in Section VIII.

VI. HEAT CAPACITY

The resemblance of the critical point to a second-order phase transition or λ -point makes relevant to the present section a vast body of work done on the heat capacity changes in order-disorder transitions.³⁹ The early approximate theories give a heat capacity which rises to a finite maximum as the temperature is raised to T_c and then drops abruptly with no "tail" at all, or a very slight one, to a relatively constant value as the temperature is raised above T_c . The absence of a tail in the heat capacity curve is certainly due to the assumption in these approximate series that the long-range order vanishes sharply at T_c . Of course, it is true that the range of order is infinite at temperatures below T_c , and finite above, but what is assumed is that the range of order above T_c extends only over a few near neighbours. What actually happens, as a wide variety of experimental and theoretical evidence indicates, is that the range of order increases continuously and gradually as the temperature is lowered to T_c . It is just this gradually increasing order which is of interest here, and so all theories which ignore it will not be considered.

On the experimental side, one of the most interesting features of heat capacity measurements in the critical region is the difference in behavior between a stirred and an unstirred system. Amirkhanov^{2,3} found that the sharp rise in heat capacity of a water-phenol mixture in the critical region was not observed if the mixture was stirred. He explained this change in behavior as due to the large temperature gradients which were observed in the absence of stirring, and asserted that the large viscosity in the critical region resulted in much less convection than in a normal liquid. The actual viscosity changes are not large enough to make this explanation likely, and the explanation is, in any event, not applicable to adiabatic experiments¹¹⁰ or to sound dispersion experiments,⁸⁷ but it does point up the difficulty of measurements in the critical region. To stir or not to stir is a difficult question to answer. It is not always clear whether stirring will take the system closer to equilibrium or farther away, since many of the observed phenomena depend on the existence of long-range correlations which should be very sensitive to mechanical disturbance. The rate of equilibration of a disturbed system in the critical region may vary widely. Murray and Mason⁸⁴ measured the turbidity of ethylene and xenon in the critical region and found that the turbidity returned to its equilibrium value, after a mechanical disturbance, within a few minutes. On the other hand, a thermal disturbance of a critical mixture may take hours to die out.¹¹⁰ The procedure which most inspires confidence is to stir the system and then follow its behavior as a function of time.

Most heat capacity measurements have been made on binary mixtures rather than on the one-component liquids. This is doubtless due to the relative ease of finding convenient critical mixing temperatures. Some examples of binary mixture work are given in References 2, 3, 28, 29, 54, 57, 110, 115, 116, 122, and 131, and for measurements on one component see References 80 and 113.

The author's theory of the heat capacity of binary mixtures will now be considered. It has many similarities to the random phase or ring diagram approximation,¹³ but is much more intuitive in spirit and simpler in mathematical form. The formulae for the heat capacity in the critical region are essentially identical, but the present method avoids the necessity of specifying the

intermolecular potential, and one aspect of consistency, identity of the temperatures at which the heat capacity and compressibility become infinite, is assured from the beginning. On the other hand, the theory is not at all complete in the sense of arriving at an expression for the free energy as a function of temperature and composition. Attempts to develop the theory to such a stage of completion would doubtless reveal many inconsistencies.

The theory, which gives the heat capacity as proportional to $(T - T_c)^{-\frac{1}{2}}$, will first be reviewed essentially in its original form.³⁶ Then alternative derivations and possible generalizations will be considered. Suppose that it is possible to define an entropy density, that is an entropy per unit volume, at each point in a system of nonuniform composition. This is an impossible object if the composition variation is specified in too great a detail, e.g., by specifying the position of each molecule, for the entropy is characteristic of the ensemble distribution; a system specified in maximum detail has zero entropy. Still, if the specified variation of composition is less extreme, an entropy definition should be possible. The system might be divided up into cells, each containing a great many molecules, but with the composition differing slightly from one cell to an adjoining one. In this situation a conventional entropy can be defined and calculated for each cell; it is just the entropy of mixing for the specified composition. An equivalent procedure is to expand the composition as a function of position in a Fourier series or integral, but with the suppression of all Fourier components having a wave number greater than some $k_{\max}$.

If the fluctuation in the local volume fraction of component 2 in a binary mixture is denoted by $\delta\varphi_2$ the fluctuation in entropy density is

$$\delta s = (2\varphi_2 V_1)^{-1} (\partial^2 \mu_1 / \partial \varphi_2 \partial T)_P (\delta \varphi_2)^2 \quad (74)$$

If a Flory-Huggins chemical potential is used the entropy fluctuation has the form

$$\delta s = -\frac{1}{2} k_B [(V_1 \varphi_1)^{-1} + (V_2 \varphi_2)^{-1}] (\delta \varphi_2)^2 \quad (75)$$

and the fluctuation is, of course, negative. According to the assigned interpretation of $\delta\varphi_2$,

$$\delta \varphi_2 = \int_{k_{\max}}^{\infty} \varphi_k e^{i\mathbf{k} \cdot \mathbf{R}} d\mathbf{k} \quad (76)$$

where the symbol on the integral indicates that the absolute value of k in the integration should not exceed a maximum value. This maximum value might reasonably be of the order $(10 \text{ \AA})^{-1}$, but the heat capacity results turn out to be independent of the value chosen. The entropy given in Eq. (75) is proposed to apply to a given state of entropy production, that is for a given set of φ_k , $k \leq k_{\max}$. The ensemble average of this entropy requires the evaluation of $\langle \varphi_k \varphi_{k'} \rangle$. This is just the Fourier transform of

$$\langle \delta \varphi_2(R_1) \delta \varphi_2(R_2) \rangle \quad (77)$$

Now the changes with composition of the partial molecular volumes are being neglected, so $\delta \varphi_2 = V_2 \delta n_2$, and the correlation between fluctuations in volume fraction at two points has the same form as the correlation between fluctuations in number density, which has already been discussed. For long wavelengths, or small k ,

$$\langle \varphi_k \varphi_{k'} \rangle = \varphi_2^2 G_k \delta(\mathbf{k} + \mathbf{k}') \quad (78)$$

where G_k is the Fourier component of $G(r)$. Therefore,

$$\langle \delta s \rangle = (\varphi_2/2V_1)(\partial^2 \mu_1 / \partial \varphi_2 \partial T) \int^{k_{\max}} G_k d\mathbf{k} \quad (79)$$

It is interesting to observe that the only difference between the meaningful, if approximate, predictions of the equation above, and the prediction of nonsense comes in the introduction of $k_{\max}$, that is, in the introduction of spatial smoothing. Since

$$\begin{aligned} G(r) &\equiv g(r) - 1 = \int G_k e^{i\mathbf{k} \cdot \mathbf{r}} d\mathbf{k} \\ G(0) &= -1 = \int G_k d\mathbf{k} \end{aligned} \quad (80)$$

for the unrestricted integrations, their use would make Eq. (79) very uninteresting. Actually, Eq. (78) would have to be corrected if infinite k were allowed, and sharp localization of molecules would make the entropy fluctuation infinite.

The transform relations for an Ornstein-Zernike distribution function are

$$G(r) = ar^{-1} e^{-\kappa r} \quad (81)$$

$$G_k = (a/2\pi^2)(k^2 + \kappa^2)^{-1} \quad (82)$$

Since, as has already been noted, κ^2 is related to the chemical potential by the equation

$$\frac{4\pi a}{\kappa^2} = -\frac{V_1}{\varphi_2} \left[\frac{k_B T}{(\partial\mu_1/\partial\varphi_2)_{P,T}} + \frac{V_2}{V_1} \right] \quad (83)$$

one has for mixtures close to the critical point

$$\left(\frac{\partial^2 \mu_1}{\partial \varphi_2 \partial T} \right)_P = -\frac{k_B T V_1}{4\pi a \varphi_2} \left(\frac{\partial \kappa^2}{\partial T} \right) \quad (84)$$

and Eq. (79) now becomes

$$\langle \delta s \rangle = -\frac{k_B T}{16\pi^3} \left(\frac{\partial \kappa^2}{\partial T} \right) \int_0^{k_{\max}} (k^2 + \kappa^2)^{-1} d\mathbf{k} \quad (85)$$

The increment Δ to the heat capacity per unit volume, which arises because of the composition fluctuation, is, from the assumption of negligible compressibility, the same for both the constant volume and constant pressure heat capacities. Differentiation of Eq. (85) with respect to temperature gives

$$\Delta = \frac{k_B}{16\pi^3} \left(\frac{\partial \kappa^2}{\partial \ln T} \right)^2 \int_0^{k_{\max}} (k^2 + \kappa^2)^{-2} d\mathbf{k} \quad (86)$$

as the dominant term if κ^2 is proportional to $T - T_c$. Integration gives

$$\Delta = k_B (16\pi\kappa)^{-1} (\partial \kappa^2 / \partial \ln T)^2 \quad (87)$$

The predicted heat capacity increment is consequently proportional to $(T - T_c)^{-\frac{1}{2}}$, if the mixture is at the critical composition. This is a result considerably more susceptible to testing than might have been hoped for. Introduction of a short-ranged correlation length l ²³ through

$$\kappa^2 = 6(\delta T)/l^2 T_c \quad \delta T = T - T_c \quad (88)$$

for a mixture at the critical composition, and division of Δ by the molar density to give the heat capacity increment per mole gives

$$\Delta_M = R V_1 [1 + \varphi_2(m^{-1} - 1)]^{-1} (16\pi)^{-1} T_c^{\frac{1}{2}} (6^{\frac{3}{2}}/l^3) (\delta T)^{-\frac{1}{2}} \quad (89)$$

The equation is tested in Fig. 5, where the theoretical curve has the form

$$C_P = C_0 + \Delta_M = [39 + 18(T - T_c)^{-\frac{1}{2}} \text{ deg}^{\frac{1}{2}}] \text{ cal/mole deg} \quad (90)$$

C_0 being taken as constant. The theoretical curve corresponds to $l = 4.9 \text{ \AA}$, a quite reasonable value although not in good agreement with Zimm's light-scattering measurements.³⁶ Heat

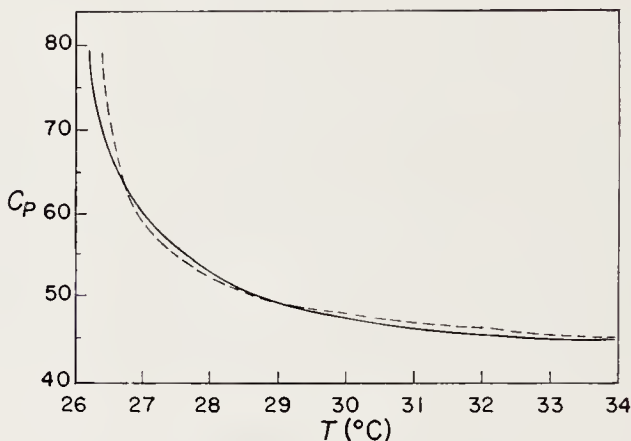


Fig. 5. The experimental (solid curve) and theoretical (dashed curve) heat capacities in cal/mole deg of the mixture C_7F_{14} - CCl_4 at the critical composition in the critical region. [After Fixman, M., *J. Chem. Phys.* **36**, 310 (1962).]

capacity measurements on the iso-octane-perfluoroheptane system, previously used to test the viscosity theory, also exist,⁵⁴ and the supercritical data are fitted excellently by

$$C_P = \left[100 + \frac{9}{(T - 23.5)^{\frac{1}{2}} (\text{deg})^{\frac{1}{2}}} \right] \text{ cal/mole deg} \quad (91)$$

The choice of coefficient corresponds to $l = 7.1 \text{ \AA}$. It should be noted that T_c was quoted as 23.16°C , while it has been necessary to use $T_c = 23.5^\circ\text{C}$ to fit the data with the expression above. Since a temperature differential of 0.3°C was used for T near T_c , the data near T_c are not very reliable, as the authors realized.

There are at least two alternative ways of deriving Eq. (87) or something very similar. Zaitsev¹³⁸ has used the Ornstein-Zernike distribution function in the formula for the internal energy. There is evidently an energy contribution of the form

$$\int V(r)r^{-1} e^{-\kappa r} f(r) d\mathbf{r} \quad (92)$$

where $V(r)$ is an intermolecular potential and $f(r)$ is a function which guards against overlap and is not very sensitive to temperature. Differentiation of this formula with respect to temperature gives a heat capacity which behaves similarly to Eq. (89). The derivation suffers from two defects. First, it relies on the behavior of the Ornstein-Zernike distribution function at small intermolecular distances, where there is no reason whatever to expect the Ornstein-Zernike formula to be valid. Secondly, the result contains parameters in the intermolecular potential and $f(r)$ which are difficult to evaluate. Zaitsev also states that his formula is invalid if the system is too close to the critical point, on the grounds that the Ornstein-Zernike formula becomes invalid there. The origin of his remark lies in the possibility that nonlinear terms may enter the equations which determine the Ornstein-Zernike distribution function; this question has already been discussed in the present article.

Still another heuristic derivation of Eq. (86) follows from a partial integration of the configuration integral over the molecular coordinates. One can proceed as in Kirkwood's derivation of the cell model (Reference 48; page 358). Divide the system into N cells, each large enough to contain a large average number of molecules. If n_i is the number of molecules in cell i , then the configurational free energy and configuration integral are given by

$$e^{-A/k_B T} = Z = \sum_{m_i=0}^{N_0} \frac{N!}{m_1! \dots m_N!} Z(m_1 \dots m_N) \quad (93)$$

$$\sum_{i=1}^N m_i = N_0$$

where N_0 is the total number of molecules and $Z(n)$ is the configuration integral for a system in which there are m_i molecules in cell i . In the critical region the existence of long-range correlations implies that Z cannot be a product of configuration

integrals, one for each cell. Rather it must include the effect of the interaction between, at least, neighboring cells. If the change in n_i is small enough from cell to cell, one can write this sum, if the system is close enough to the critical point, as

$$e^{-A/k_B T} = K \int_{m_i=0}^{N_0} \int \exp \left\{ -\text{const.} \int [\kappa^2 n^2 + |\nabla n|^2] d\mathbf{R} \right\} dm_1 \dots dm_N \quad (94)$$

where K is presumed to be constant in the critical region and n is the fluctuation in concentration at a given point. Terms linear in n in the exponential vanish by virtue of the constraint that the system is closed. The gradient term in the exponential represents the simplest possible interaction between cells, after the number of molecules in each cell has been smoothed out into a continuous distribution. The set of numbers m_i is related to the Fourier components n_k by a linear transformation. Thus

$$m_i = \sum_{k_l} \int n_k \exp (i\mathbf{k}_l \cdot \mathbf{R}) d\mathbf{R} \quad (95)$$

where the space integral runs over the i th cell. Introduction of this transformation into Eq. (94) and integration over the n_k gives

$$e^{-A/k_B T} \propto \prod_{l=0}^{l_{\max}} (k_l^2 + \kappa^2)^{-\frac{1}{2}} \quad (96)$$

The dominant term in the entropy of the system in the critical region is obtained from this free energy as

$$S = -\frac{1}{2} k_B T \left(\frac{\partial \kappa^2}{\partial T} \right) \sum_{l=0}^{l_{\max}} (k_l^2 + \kappa^2)^{-1} + S_0 \quad (97)$$

A boundary condition establishes possible values of k_l as

$$(k_l)_x L = l_x \pi \quad l_x = 0, 1, \dots \quad (98)$$

and similarly for the y and z components, if the whole system is in a cube of side L . Conversion of the sum in Eq. (97) into an integral then gives Eq. (85).

This same analysis can be carried through in two dimensions, but unfortunately leads to a physically unreasonable result.

Onsager⁹⁰ evaluated the mean range of order, κ^{-1} , in the critical region, although only for an Ising lattice in the absence of an external magnetic field, which corresponds to a binary mixture at the critical composition. It turned out that

$$\kappa^2 \propto (T - T_c)^2 \quad (99)$$

and if this relation with the appropriate proportionality constant is used the heat capacity turns out to be proportional to $\ln(T - T_c)$. However, the latter proportionality constant, although it has the correct magnitude, has the wrong sign. This strange result is not too surprising, since it was found in the theory of the critical correlation function that physically sensible results could be obtained only by taking into account high powers of the composition fluctuation in the expression for the local free energy. In the theory of the heat capacity, as in the theory of $g(r)$, there are striking differences between two and three dimensions.

Although there are no exact results to compare with the three-dimensional heat capacity, tentative extrapolations of high-temperature series have indicated that²⁶

$$C_V/k_B \propto (1 - T_c/T)^{-1/b} \quad b \geq 4 \quad (100)$$

and that the heat capacity at the critical point is certainly infinite. Probably C_V diverges logarithmically (private communication from G. A. Baker, Jr.).

VII. SOUND PROPAGATION

It is a truism that the theory of irreversible processes is more difficult and less general than the theory of equilibrium states. However, it happens on occasion that the theory of an equilibrium quantity is so rudimentary that a generalization of the theory to dynamic measurement seems straightforward and almost inevitable. This situation occurs in the present theory of the heat capacity, which is taken as the basis of a theory of anomalous sound propagation in the critical region.

There are several reasons for thinking that the heat capacity is the proper function to be studied in an explanation of the anomalous effects. It is first necessary to rule out an explanation

based on the usual macroscopic theory in which absorption is accounted for in terms of the macroscopic viscosities and heat conductivity. The macroscopic theory, which has been thoroughly studied by Truesdell,¹³⁰ is certainly grossly inadequate for explaining the large absorption if typical values of the viscosity and heat conductivity are used. It is true that the shear viscosity of critical mixtures has an unusually large value, but this increase over normal values rarely exceeds a factor of 2 and is inadequate by several powers of 10 to explain the results. Not enough is known about the bulk viscosity to be completely certain about its effects, but simple theories indicate similar orders of magnitudes for the first and second viscosity coefficients, and these magnitudes are too small to be relevant. The author knows of no experiments which indicate a sufficiently large thermal conductivity in the critical region; indeed, experiments indicate a sluggish response to a thermal perturbation, although this seems to be due to the large heat capacity. However, this subject should be looked into more closely.

A macroscopic explanation being abandoned, it becomes necessary to suppose that one or more of the thermodynamic quantities which enter into the sound equations is frequency-dependent. An early theory³⁴ was based on the intuitively attractive notion that different regions of the system would have different local heat capacities because of density or composition fluctuations, and that consequently the passage of a sound wave would alter the temperatures of the different regions differently; the process of temperature equilibration between these regions would then absorb energy from the sound wave. Unfortunately, this idea^{34,37} predicted too small an absorption. This approach could have been, but was not, formulated in terms of a frequency-dependent heat capacity. The term investigated was linear in both the temperature variation of the sound wave and the density or composition fluctuation of the system. Higher-order fluctuations were neglected. A later attempt to deal with the square of local fluctuations in a theory of the heat capacity³⁶ which has been described previously turned out to be moderately successful, and the generalization to a rapid temperature variation, which is necessary for a treatment of sound waves, is relatively simple.

The experimental measurements available, in References 1, 8, 19, 20, and 121, for example, seem adequate for rough checks of rough theories, but measurements which are both extensive and precise are not very common.

The derivation of the entropy in terms of the long-wavelength composition fluctuations seems to need no generalization to time-dependent temperature variations. However, the composition correlations which appear in the entropy expression will not respond fully and in phase with a rapid temperature variation, and a computation of this response is now necessary for a computation of the dynamic heat capacity. It will be supposed, as in the theory of the viscosity, that the radial distribution function satisfies the generalized diffusion equation

$$-\frac{dG}{dt} = h[\kappa^2 \nabla^2 G - \nabla^2 \nabla^2 G] \quad (101)$$

The interaction between G and the temperature variation of the sound wave is taken to occur at the same point in this equation as in the theory of the static heat capacity; that is, at κ^2 . For a sound wave of frequency ω ,

$$\kappa^2 \rightarrow \kappa^2 + \frac{\partial \kappa^2}{\partial T} (\delta T) \quad (102)$$

$$\delta T = T_\omega e^{i\omega t} \quad (103)$$

The variation of δT with position may be neglected, since the sound wavelength is much larger than the range of correlations at controllable temperature intervals from the critical point. Only a first-order perturbation theory will be attempted, so when Eq. (102) is used in Eq. (101) the equilibrium G may be used where it multiplies δT . If $G_k^{(1)}$ is the perturbation in G induced by the sound wave, we have

$$i\omega G_k^{(1)} = h k^2 (k^2 + \kappa^2) + h k^2 \frac{\partial \kappa^2}{\partial T} G_k^{(0)} T_\omega \quad (104)$$

Equation (104) is readily solved for the perturbation, and on substitution into the previous expression for the entropy gives a dynamic heat capacity.

$$\Delta = T \frac{\langle \delta s \rangle}{\delta T} \quad (105)$$

$$= k_B \left(\frac{\partial \kappa^2}{\partial \ln T} \right)^2 (4\pi^2)^{-1} (h/\omega)^{\frac{1}{2}} f(d) \quad (106)$$

$$f(d) = d^{-\frac{1}{2}} \int_0^{\infty} w^4 (w^2 + 1)^{-1} [-id^{-2} + w^2(w^2 + 1)]^{-1} dw \quad (107)$$

$$d \equiv \kappa^2 (h/\omega)^{\frac{1}{2}} \quad (108)$$

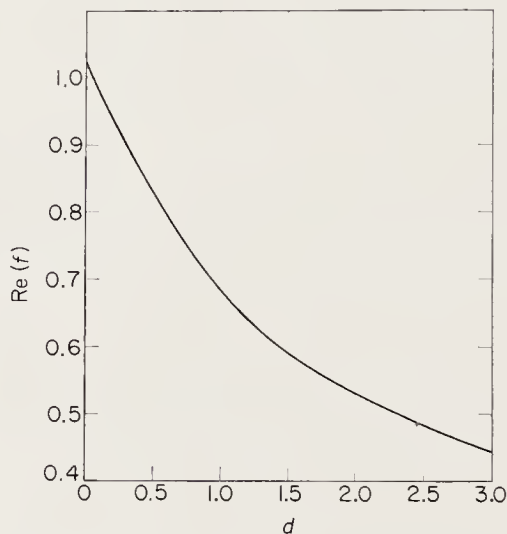


Fig. 6. The real part of the function $f(d)$, which is proportional to the dispersion, is graphed against d . [After Fixman, M., *J. Chem. Phys.* **36**, 310 (1962).]

Although a closed expression for the integral in Eq. (107) can be derived, it is not very useful; numerical integrations of the real and imaginary parts of f are shown in Figs. 6 and 7. Close to the critical point the following expansions are useful:

$$\text{Im}(f) = 0.425 - 1.28d + 1.57d^{\frac{3}{2}} + \dots \quad (109)$$

$$\text{Re}(f) = 1.026 - 0.531d + \dots \quad (110)$$

Both the real and imaginary parts of the dynamic heat capacity are finite at the critical point and become larger with decreasing frequency. The dependence on frequency is extremely small at the critical point, as Eqs. (106), (109), and (110) show. The dependence will be even smaller in the immediate neighborhood of the critical point, since the multiplying factor in Eq. (106)

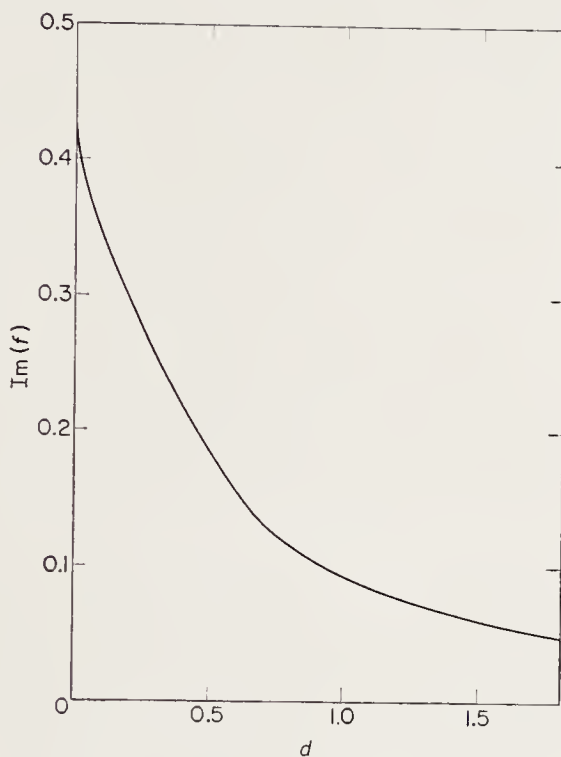


Fig. 7. The imaginary part of the function $f(d)$, which is proportional to the absorption, is graphed against d . For a mixture at the critical composition, $d \propto (T - T_c)$. [After Fixman, M., *J. Chem. Phys.* **36**, 310 (1962).]

increases with decreasing frequency, while f decreases with decreasing frequency. For a critical mixture of small compressibility, the effect of composition fluctuations on sound propagation is most easily obtained through the introduction of a complex speed of sound, C_c . A sound wave propagating along the x axis has an amplitude varying as

$$\exp [\omega C_c^{-1} x - i \omega t] \quad (111)$$

where

$$C_e = C_T \gamma^{\frac{1}{2}} \quad (112)$$

$$\gamma = C_P/C_V \quad (113)$$

and C_P and C_V are the heat capacities per mole at constant pressure and constant volume respectively. These heat capacities are assumed to have values denoted by a superscript zero in the absence of critical fluctuations, and are given by

$$C_P = C_P^0 + \Delta_M \quad C_V = C_V^0 + \Delta_M \quad (114)$$

To the lowest order in the perturbations, the complex speed of sound is given by

$$C_e = C_0 [1 - (\Delta_M/2C_P^0)(\gamma_0 - 1)] \quad (115)$$

where

$$C_0 = C_T \gamma_0^{\frac{1}{2}} \quad \gamma_0 = C_P^0/C_V^0 \quad (116)$$

The absorption is commonly recorded as the difference in the logarithms of the sound amplitudes at two points a wavelength apart. The absorption per wavelength turns out to be

$$\alpha_\lambda = \pi H \mathcal{J}(f) \quad (117)$$

$$H \equiv (\gamma_0 - 1)(R/C_P^0)(\partial \kappa^2 / \partial \ln T)^2 (n_1 + n_2)^{-1} (4\pi^2)^{-1} (h/\omega)^{\frac{1}{2}} \quad (118)$$

As was previously noted in the theory of viscosity, h may be expressed in terms of common parameters. If C is the real part of the speed of sound,

$$(C - C_0)/C_0 = -\frac{1}{2} H \operatorname{Re}(f) \quad (119)$$

An experimental test of these equations requires additional parameters over those which have been used before. The correlation distance l will be required again and also the friction constant β , but an evaluation of H also requires a knowledge of γ_0 and C_P^0 . These can probably be estimated with fair reliability for the system n-hexane + aniline for which the attenuation and dispersion were measured by Chynoweth and Schneider.²⁰ Both components have heat capacities close to 50 cal/mole deg, and one can reasonably take this value for the mixture. The approximate empirical rule⁴⁶ that $C_P^0 - C_V^0 \cong 5R$ allows an estimate of

C_V^0 . With the parameters $\beta = 9 \times 10^{13} \text{ sec}^{-1}$, and $l = 4 \text{ \AA}$, the theoretical solid curve of Fig. 8 is obtained. The agreement is quite satisfactory and the values of the parameters seem quite reasonable, although l should perhaps be somewhat larger and β somewhat smaller. The theoretical curves are considerably more sensitive to the value of l than β , so that the value of β is not very well established.

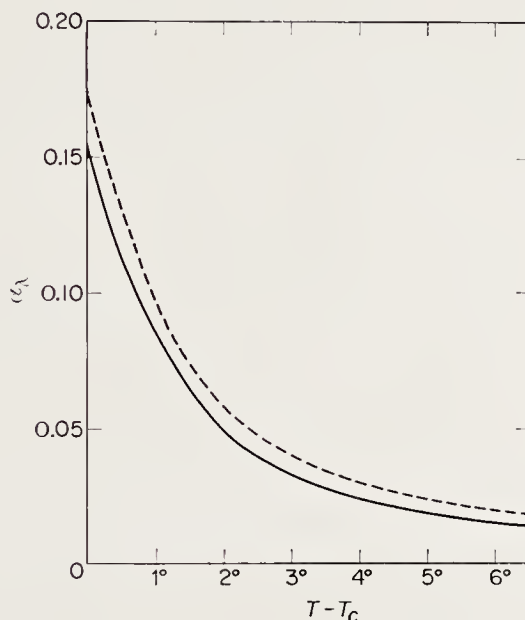


Fig. 8. Absorption per wavelength against $T - T_c$ in $^{\circ}\text{C}$. Dashed curve experimental, solid curve theoretical. Mixture aniline + n-hexane at the critical composition. [After Fixman, M., *J. Chem. Phys.* **36**, 310 (1962).]

It should be mentioned that the data of Chynoweth and Schneider have been taken in Fig. 8 to measure the attenuation of the sound amplitude rather than the sound intensity. The theory of their experimental method is extremely intricate, and the authors were not able to apply it fully. However, the simplest interpretation of their method makes their numbers refer to intensity attenuation, and the values of α_λ in Fig. 8 should be halved. The optimum parameters are then $l = 5 \text{ \AA}$, $\beta = 3.4 \times 10^{13} \text{ sec}^{-1}$.

Both the predicted and experimental dispersions are so small that no very useful comparison can be made. Theory indicates that the speed of sound should rise about 3% when the temperature is raised 5° above the critical point, while experiment gives a rise about half as great. Effects this small are obviously impossible to disentangle from a normal temperature variation.

VIII. MISCELLANY

Several areas that seem on the one hand to be lacking either experimental or theoretical work, or on the other hand seem quite settled, such as binary diffusion, are briefly commented on here.

A. Diffusion

It has been assumed, whenever relevant in this review, that the binary diffusion constant $D(T)$ vanishes at the critical mixing point, and the evidence for this assumption seems incontrovertible.^{22, 61, 63, 73, 74, 124} It has also been assumed that $D(T)$ vanishes proportionately to the derivative of the chemical potential with respect to concentration, and this appears to be correct.¹²⁴ But finally, it has been assumed that $D(T)$ vanishes proportionately to $T - T_c$, and this is not so well established, either experimentally or theoretically. Experimental evidence exists for the proportionality,^{73, 74} and against;²² data in the latter reference indicate that $\partial D/\partial T$ is becoming large at the critical point. In classical thermodynamics it is usually assumed that the concentration derivative of the chemical potential, and therefore $D(T)$, is proportional to $T - T_c$ in the critical region. However, extrapolations of series solutions to the Ising problem, previously alluded to, give a magnetic susceptibility which becomes infinite more rapidly than $(T - T_c)^{-1}$. In the language of a binary mixture, this means that the derivative of the chemical potential, and $D(T)$, should vanish more rapidly than $(T - T_c)$, or $\partial D/\partial T$ should vanish at the critical point. This has not been observed.

There is considerable evidence that the thermal diffusion ratio becomes very large in the critical region.^{18, 42, 97, 127, 128} It is possible, but not certain, that the anomaly can be ascribed solely to the vanishing of $D(T)$.¹²⁷

B. Sound Propagation in Gases

The theory of sound propagation and attenuation in the critical region of a gas is considerably more difficult than the corresponding problem for liquid mixtures. Although the heat capacity theory given here can easily be modified, the other requirement for the dynamic equations which govern the relaxation of the radial distribution function is less easily achieved. There is no simple analog to the diffusion equation; rather a coupled pair of equations, one for momentum transfer and one for energy transfer, are required. Landau and Placzek^{40,52,67} have performed an *ad hoc* simplification of these equations into a "pressure" wave and an "entropy" wave, the latter governing critical fluctuations, but whether a detailed analysis will justify their simplification remains to be seen. W. Botch and the author are investigating this point. There are ample ultrasonic measurements to be tested.^{12,21,71,88,89,111,126,129}

C. Viscosity and Thermal Conductivity of Gases

It is not yet certain whether the viscous behavior of a gas and of a liquid mixture are similar in their respective critical regions. Michels⁷⁹ has found maxima in graphs of the viscosity against density at temperatures above T_c , but because of the large compressibility in the critical region the capillary-flow experiments are inconclusive. Naldrett and Maass,⁸⁵ in their oscillating disk measurements of η vs. T for CO_2 , found that the gas viscosity rises sharply but smoothly as the temperature is lowered to T_c , and connects without change of slope onto the curve of $\eta(\text{liquid})$ vs. T . Schneider¹¹² has asserted that if the vapor rather than the liquid viscosity had been measured for $T < T_c$, the viscosity-temperature graph would have shown a sharp maximum at the critical point. This conjecture may well be correct, but the smooth connection between gas and liquid viscosities makes interpretation difficult.

The thermal conductivity of gaseous CO_2 definitely seems to show a large maximum at the critical point.^{120a} After Sengers' and Michels' careful work, an explanation based on experimental artifacts such as convection would be difficult to sustain.

D. Dielectric Behavior

Both the dielectric constant and dielectric loss show peaks at the critical mixing temperature of a binary mixture.¹¹⁴ This evidence indicates anomalies in orientational correlations and relaxation in the critical region, but how the orientational correlations are related to composition correlations (which more generally characterize the critical region) is unknown.

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THE EQUATION OF STATE OF THE CLASSICAL HARD SPHERE FLUID

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I. INTRODUCTION

Basic questions of the equilibrium theory of fluids are concerned with: (1) an adequately detailed description of the emergence of a fluid phase from a solid or the transition between a liquid and its vapor, the phase transition problem, and (2) the prediction from "first principles" of the bulk thermodynamic properties of a fluid over the whole existence region of the fluid. We will consider primarily the second of these questions. All bulk thermodynamic properties of monatomic fluids follow from a knowledge of the equation of state. This chapter will review certain recent developments in the approximate elucidation of the equation of state of a particularly simple fluid, the classical hard sphere fluid. This fluid is composed of "identical" particles or molecules, obeying classical mechanical laws, which are rigid spheres of diameter a . Two such molecules interact with one another only when they collide elastically.

The importance of this model is due to the considerable mathematical simplifications in the many-body problem theory resulting from its use as well as its usefulness in describing the behavior of real fluids under extreme conditions. Thus, at very high temperatures, when the average kinetic energy of a gas molecule is much greater than the minimum value of the intermolecular potential energy, the hard core (of diameter a) of this potential energy is all important in determining the properties of the fluid. At very high densities, on the other hand, the attractive part of a more realistic intermolecular potential energy can be thought of as a smooth average potential not greatly affecting the properties of the fluid.

Hard sphere theories can be compared in a special sense with "experiment". This is not because any real substance possesses a fluid phase which over its whole existence region could be adequately described by this simple model. The "experimental data," rather, are the result of extensive machine calculations of the equation of state of large collections of hard spheres undertaken by Alder and Wainwright¹ and Wood, Parker, and Jacobson,² among others.

A considerable portion of this chapter will be devoted to an exposition of the "scaled particle theory" approach^{3,4} to this model system (Section V). The hard-sphere-fluid equation of state obtained through this approach represents quite well the machine-computed data over the whole region of stability of the fluid phase.^{3,5} An important pedagogic advantage of this theory is that each of the successive steps of its argument are easily motivated by physical intuition. Disregarding for the purposes of this review certain questions of rigor, our simple mathematical development is essentially self-contained and presumes no further familiarity with statistical mechanics beyond the content of a typical introductory text.⁶ Section II deals with the statistical mechanical description of a simple fluid, i.e., a fluid of spherical molecules interacting with one another as a result of central forces between the molecules. To provide a setting for subsequent developments, Section III reviews very briefly various current theoretical approaches to fluids. Needless to say, even if we had wanted to do justice to these, considerations of space would have precluded our doing so. In any case, excellent reviews of these

theories exist in the literature.⁷⁻¹¹ Section IV is concerned with the hard sphere system; we have collected some exact results and we describe the phase diagram resulting from the machine-computed data. Section V deals with the theory of the equation of state of the hard sphere fluid in one, two and three dimensions. In the final section we make some concluding remarks about some of the many open problems in this field and indicate some applications of the foregoing theory to real systems, without going into the details of these applications.

II. THE STATISTICAL DESCRIPTION OF A SIMPLE FLUID

We consider a macroscopic sample of a simple fluid in thermodynamic equilibrium with its surroundings at the absolute temperature T . The simple fluid sample consists of a number, N , of (identical) spherically symmetric molecules, held in a rigid container of volume V , which interact with pairwise central forces. Thus the mutual forces between two molecules centered at $\mathbf{r}_i$ and $\mathbf{r}_j$ are derivable from a potential $\varphi(r_{ij})$ which is a function of the distance $r_{ij}(r_{ij} = |\mathbf{r}_i - \mathbf{r}_j|)$ between the centers of the two molecules. The total intermolecular potential energy is obtained by summing contributions over all pairs:

$$U = \frac{1}{2} \sum_{i=1}^N \sum_{\substack{j=1 \\ i \neq j}}^N \varphi(r_{ij}) \quad (1)$$

which we note is a symmetric function in the $\mathbf{r}_i$. The only other forces which act on the molecules are caused by interactions with the rigid walls of our container. In what follows we need take account of these only by suitably restricting the regions of spatial integrations to be within the volume V . We are interested in the bulk thermodynamic properties of the fluid, e.g., the equation of state of the fluid. This allows us to simplify certain of our subsequent formulas by taking the limit as both N and V approach infinity in such a manner that the number density ρ , $\rho = N/V$, remains finite but terms $O(1/N)$ or $O(1/V)$ can be neglected. Such terms will not even be explicitly exhibited in what follows.

Under very general conditions, it follows from classical statistical mechanics that the equilibrium behavior of our fluid system is adequately described by the behavior of a Gibbsian ensemble of systems characterized by a canonical distribution (in energy) in phase space.^{6,9-11} This has two immediate consequences. First it specifies the spatial distribution of our N molecule system. The simultaneous probability that some first molecule center lies in the volume element $d\mathbf{r}_1$ whose center is at $\mathbf{r}_1$ and etc., and the N th molecule center lies in the volume element $d\mathbf{r}_N$ whose center is at $\mathbf{r}_N$ is

$$P\{\mathbf{r}_1, \dots, \mathbf{r}_N\}d\mathbf{r}_1 \dots d\mathbf{r}_N \\ = \exp \left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N / Q_N \quad (2)$$

where the normalization constant Q_N is the so-called configurational partition function, the calculation of whose value is the central mathematical problem of classical statistical mechanics,*

$$Q_N = \int \dots \int_V \exp \left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N \\ = V \int \dots \int_V \exp \left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(r_{ij}) \right] d\mathbf{r}_2 \dots d\mathbf{r}_N \quad (3)$$

since $\exp[-U/kT]$ is a function only of the r_{ij} . Secondly, the virial theorem applies; this is an immediate consequence of the equipartition principle, as an integration by parts shows. This allows us to compute the pressure p of our fluid, which is defined as the normal stress exerted by the fluid on a plane rigid wall.

The virial theorem tells us that the average value of the kinetic energy of our fluid, $\frac{3}{2}NkT$ is equal to minus one half of the average value of the virial, i.e., the sum over all molecules of the product $\mathbf{r}_i \cdot \mathbf{F}_i$, where $\mathbf{F}_i$ is the total force on the i th molecule. This total force can be split into contributions arising from interactions with

* The reduction in Eq. (3) is only asymptotically correct for fluids, not for solids.

the rigid walls, which give rise to a term $\frac{3}{2}pV$, plus the intermolecular contributions. Rearranging slightly, the pressure of the fluid can be written as⁶

$$p = \rho kT - \frac{2\pi}{3} \rho^2 \int_0^\infty \frac{d\varphi}{dr} g(r) r^3 dr \quad (4)$$

where $r = r_{12}$ and $\frac{1}{2}\rho g(r)r^2 dr$ is the average number of pairs of molecules separated by the distance r . The pair correlation function $g(r)$ is thus simply related to the conditional probability density $\rho g(r)$ that another molecule center can be found within a spherical shell of radius r and thickness dr from the center of a given fixed molecule. For a sufficiently large system ($N, V \rightarrow \infty$, $N/V = \rho < \infty$), $g(r)$ follows from Eq. (2) as

$$g(r_{12}) = V^2 \int \dots \int_{\mathbf{r}}^{(N-2)} \exp \left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(r_{ij}) \right] d\mathbf{r}^3 \dots d\mathbf{r}_N / Q_N \quad (5)$$

Its occurrence in Eq. (4) rather than the higher-order correlation functions

$$g_n(\mathbf{r}_1 \dots \mathbf{r}_n) \quad (n \geq 3)$$

where

$$\begin{aligned} g_n(\mathbf{r}_1 \dots \mathbf{r}_n) \\ = V^n \int \dots \int_{\mathbf{r}}^{(N-n)} \exp \left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(r_{ij}) \right] d\mathbf{r}_{n+1} \dots d\mathbf{r}_N / Q_N \end{aligned} \quad (6)$$

is a direct consequence of the pairwise nature of the forces acting between the molecules. Using $g(r)$, other thermodynamic properties of our system such as, for example, the internal energy (the caloric equation of state) can be expressed in terms of T, ρ and the molecular parameters arising in φ .^{9,10}

III. REVIEW OF OTHER THEORIES OF FLUIDS

The explicit evaluation of Q_N or $g(r)$ presents as yet unsurmounted difficulties. The only three-dimensional system for which $g(r)$ is known exactly is the trivial case of an ideal gas, for which $\varphi = 0$, $g(r) = 1$ and $p = \rho kT$. Both $g(r)$ and Q_N are known

exactly for a number of one-dimensional fluids,⁹ e.g., the exponential model of Kac¹² and the one-dimensional analog of a hard sphere fluid.^{13,14} An interesting, exactly solvable model of an electrically charged fluid resulting from the one-dimensional interaction of plane, parallel charge sheets has been studied by Lenard.¹⁵ The equation of state of one-dimensional fluid molecules interacting only with their nearest neighbors can easily be found under quite broad conditions on the intermolecular potential.⁹

In general, though, we have to resort to approximate methods. Most of these fall, roughly speaking, into three categories.⁶⁻¹¹

A. Power Series Methods

One develops, e.g., p or $g(r)$ [and thus p via Eq. (4)] into a power series in ρ . This leads to the van der Waals virial expansion for the pressure

$$p = \rho kT \left[1 + \sum_{n=1}^{\infty} B_{n+1} \rho^n \right] \quad (7)$$

where the virial coefficients B_n are closely related to the Mayer¹⁶ irreducible cluster integrals β_{n-1} ¹⁰

$$B_n = - \frac{n-1}{n} \beta_{n-1} \quad (8)$$

Each of these integrals β_{n-1} involves n volume integrations of an integrand $S'_{1,2,\dots,n}$ involving the locations of n molecules, consisting of certain products of functions $f_{i,j}$

$$f_{i,j} = e^{-\beta q(r_{ij})} - 1 \quad (9)$$

e.g., $S'_{1,2} = f_{1,2}$, $S'_{1,2,3} = f_{1,2}f_{1,3}f_{2,3}$, etc., and

$$\beta_{n-1} = \frac{1}{n!V} \int \cdots \int_V S'_{1,2,\dots,n} d\mathbf{r}_1 \cdots d\mathbf{r}_n \quad (10)$$

To visualize the terms involved in $S'_1, \dots, S'_n$ one associates with each term a formal *diagram*¹⁷ consisting of (labeled) circles for the molecules and a line segment between the i th and j th circle for each factor $f_{i,j}$ which occurs in the term. An irreducible cluster is defined as any product of $f_{i,j}$'s associated with a doubly connected diagram, and $S'_1, \dots, S'_n$ is the sum of all the different products of $f_{i,j}$'s that connect molecules $1, \dots, n$ into an irreducible cluster. In a doubly connected diagram there are at least two entirely independent paths which do not cross at any circle between each pair of molecules (circles) in the diagram.

The difficulty of evaluating or even studying the asymptotic dependence of the β_n as n increases limits the usefulness of Eq. (7) to sufficiently dilute fluids (gases). Only in the case of hard sphere molecules have the first four virial coefficients been calculated correctly analytically. Not even the sign is known, with certainty, for a virial coefficient higher than the fifth of a three-dimensional non-ideal fluid. Still, in the hands of Mayer and his collaborators^{10,16} and others^{18,19} these methods have been used as powerful tools for the investigation of phase transitions. An alternative powerful power series treatment of phase transitions has been developed by Yang and Lee.²⁰

B. Integral Equation Methods

The conservation of density of a mechanical system in phase space (Liouville's theorem)⁹⁻¹¹ implies a rigorous functional relation between $g(r_{12})$ and $g_3(r_{12}, r_{13}, r_{23})$.²¹⁻²⁴ Starting from this rigorous functional relation (an integro-differential equation*) an approximate closed equation can be obtained²¹⁻²³ by using the superposition approximation²³ which asserts that

$$g_3(r_{12}, r_{13}, r_{23}) = g(r_{12})g(r_{13})g(r_{23}) \quad (11)$$

* The equation is

$$\frac{\partial \ln g(\mathbf{r}_1, \mathbf{r}_2)}{\partial \mathbf{r}_1} = -\beta \frac{\partial \varphi(|\mathbf{r}_1 - \mathbf{r}_2|)}{\partial \mathbf{r}_1} \beta \rho \int \frac{\partial \varphi(|\mathbf{r}_1 - \mathbf{r}_3|)}{\partial \mathbf{r}_1} \frac{g_3(\mathbf{r}_1, \mathbf{r}_2, \mathbf{r}_3)}{g(\mathbf{r}_1, \mathbf{r}_2)} d\mathbf{r}_3.$$

When any one of the three molecules is outside the range of forces exerted by the other two this assumption is strictly valid.* Also in the limit $\rho \rightarrow 0$, Eq. (11) is valid to terms of order ρ but not higher. Otherwise Eq. (11) is not exact and the assessment of the error introduced by its use, even in the qualitative behavior of the $g(r_{12})$, has not been completely established.¹⁰ In any case, the most convenient way of writing the resulting non-linear integral equation employs a coupling parameter ξ ($\xi = \xi_1$). The coupling parameter technique is a generalization²⁵ of a familiar technique used, e.g., in finding the free energy of electrolytic solutions by a charging process. One defines the vector $\xi = (\xi_1, \dots, \xi_N)$, where $0 \leq \xi_i \leq 1$, $i = 1, \dots, N$, and replaces the potential energy U of the fluid given by Eq. (1) by

$$U = \sum_{1 \leq i < j \leq N} \xi_i \xi_j \varphi(r_{ij}) = U(\xi) \quad (12)$$

A real fluid has $\xi_i = 1$ for all i (full coupling of the intermolecular forces), $U = U(1, \dots, 1)$, while for an ideal fluid, at the other extreme of coupling, $U = U(0, \dots, 0) = 0$. Q_N , given by Eq. (3), and $g(r_{12})$, given by Eq. (5), become functions of ξ if U , given by Eq. (1), is replaced in Eqs. (3) or (5) by Eq. (12). If, in particular, we set $\xi_1 = \xi$, $\xi_2 = \dots = \xi_N = 1$ in the $g(r_{12}, \xi)$ obtained by the above prescription and call the resulting function of r_{12} and ξ , $g(r_{12}, \xi)$, then the approximate (superposition) integral equation for $g(R, \xi)$ is ($R = r_{12}$)

$$\begin{aligned} \ln g(R, \xi) = & -\beta \xi \varphi(R) + \frac{\pi \rho}{R} \int_0^\infty [K(R-r, \xi) \\ & - K(R+r, \xi)] r [g(r) - 1] dr \\ g(R) = & g(R, 1) \end{aligned} \quad (13)$$

* Another superposition approximation must be exact for all one-dimensional fluids which interact only with their nearest neighbors. One can easily establish the more general result for these systems that^{9,13}

$$g_n(r_1, \dots, r_n) = \prod_{i=1}^{n-1} g(r_i, r_{i+1}).$$

This applies in particular to the one-dimensional hard sphere fluid with^{13,14}

$$g(r) = \sum_{k=1}^{\infty} A(r - ka) \left(\frac{1}{\rho^{-1} - a} \right)^k \frac{(r - ka)^{k-1}}{(k-1)!} \exp \left[-\frac{r - ka}{\rho^{-1} - a} \right]$$

with $A(x) = 0$ for $x < 0$ and $A(x) = 1$ for $x \geq 0$.

The Born–Green,²² Yvon²¹ form of the kernel is

$$K(t, \xi) = \beta \xi \int_{|t|}^{\infty} (s^2 - t^2) \varphi'(s) g(s, \xi) ds \quad (14)$$

while the Kirkwood²³ form of the kernel is

$$K(t, \xi) = -2\beta \int_0^{\xi} \int_{|t|}^{\infty} s \varphi(s) g(s, \xi') ds d\xi' \quad (15)$$

The fact that the kernels are different is a reflection of the use of the superposition approximation in both derivations. The subsequent treatment of these equations to prepare them for numerical solution has been adequately reviewed.^{9–11}

A number of integral equation approaches have been formulated which dispense with the use of the superposition approximation or similar inexact ansatz.^{7, 26–29} Currently, one of the most promising approaches is through an exact closed integral equation, satisfied by $g(r_{12})$, derived by Van Leeuwen, Groeneveld and DeBoer³⁰ among others.^{31–37} This exact integral equation for $g(r)$ is

$$\begin{aligned} \ln g(r) + \beta \varphi(r) - E(r) \\ = \rho \int [g(r_1) - 1 - \ln g(r_1) - \beta \varphi(r_1) \\ + E(r_1)] [g(r_2) - 1] d\tau_3 \end{aligned} \quad (16)$$

with

$$E(r) = \sum_{n \geq 1} \int \dots \int E_n(1, 2) \rho^n d\tau_{i_1} \dots d\tau_{i_n} \quad (17)$$

Each $E_n(1, 2)$ in Eq. (17) is an integrand whose structure can be represented by an “elementary” diagram with base points 1, 2, say. For the precise definition of these diagrams the reader is referred to Reference 30. Because of the form of $E(r)$, Eq. (16), while exact, apart from some questions of convergence of the series for $E(r)$,³⁸ hardly provides a practicable method of determining $g(r)$, since many if not all of the terms of $E(r)$ have to be computed.³⁸ $E(r)$ has so far had to be drastically approximated. The simplest procedure is to set $E(r) = 0$ in Eq. (16) [$E(r)$ contains no term linear in ρ]; this yields the so-called hyper-netted chain or convolution approximation.^{35, 37} In a second approximation, the $E'_{(1)}$ approximation, the first “elementary” diagram having two

field points is retained.^{35,37} These equations have been employed to study the asymptotic form of $g(r)$ at the critical point of a fluid^{37,38} and to obtain the first few virial coefficients of a hard sphere fluid in these approximations.³⁵ Unfortunately, at the time of writing this chapter, no numerical solutions of Eq. (16) for $g(r)$ are available for comparison with those given by the numerical solution of Eq. (13).

A different integral equation approach to the equation of state of fluids is provided by the scaled particle theory.^{3,4,39,41} Its application to the hard sphere fluid, for which it is particularly suited, will be covered in Section V. The name of the theory comes from the formal use of a coupling technique employing a distance scaling parameter in the intermolecular potential. The theory focuses attention on the reversible work which has to be expended to form a (spherical) cavity, i.e., a region devoid of molecular centers, in the fluid. This reversible work is intimately related to the chemical potential of a fluid molecule μ . Using thermodynamic identities relating the pressure to integrals of density derivatives of μ one obtains certain new, exact integral equations for the change in the reversible work of cavity formation with the volume of the cavity. These, together with certain consistency relations on this work, determine, albeit incompletely, certain features of its functional form.

C. Lattice Theories (Hole, Cell and Free Volume Theories)

These theories^{9-11,42} essentially view the fluid state as that of a highly disordered solid.¹⁴ In these more or less formal lattice theories the distinction between a gas, liquid or solid arises from the loss of localization of the molecular centers to a given cell in going from a solid to a gas. Associated with this freedom to wander is the communal entropy.¹¹ A "free volume theory" is a lattice theory in which the number of cells of the lattice is chosen to be equal to the number of molecules N , while in a "hole theory" the number of cells is larger or equal to N and each cell can only be occupied by a single molecular center.¹⁰ In the simplest cell theory⁴³ the proximity of molecules to one another imprisons any given molecule in a cage formed by the cooperatively acting intermolecular forces of its neighbor molecules for much of the

time. The average volume of this cell (or cage) is the free volume, which may differ considerably from ρ^{-1} .

Space will not permit us to review the extensive literature of these theories, including the many recent developments. Instead, we shall try to apply the free volume concept to the hard sphere system in the simplest fashion. Imagine that the diameter a of the N hard spheres in the volume V of our system is shrunk till the molecules are elastic point centers. We now have an ideal gas whose Helmholtz free energy is^{6,10} ($v = \rho^{-1}$)

$$\begin{aligned} A &= -N\beta^{-1} \ln (e/\rho\Lambda^3) = +N\beta^{-1} \ln \rho + \text{constant} \\ &= -N\beta^{-1} \ln v + \text{constant} \end{aligned} \quad (18)$$

where Λ is the mean, thermal, de Broglie wavelength and where any density-independent term is treated as a constant. If this ideal gas had been separated by hypothetical partitions into N cells of average volume ρ^{-1} in which the molecules are free to move, we would have instead of (18)^{6,10}

$$\begin{aligned} A &= -N\beta^{-1} \ln (1/\rho\Lambda^3) = +N\beta^{-1} \ln \rho + \text{constant}' \\ &= -N\beta^{-1} \ln v + \text{constant}' \end{aligned} \quad (19)$$

The density dependence of A remains unchanged as we go from the gas to the idealized solid. The difference between Eqs. (18) and (19), due to the localization of each molecular center to a singly occupied cell, arises from the factor e in the logarithm of Eq. (18) and corresponds to a communal entropy of this model system of Nk . To obtain the simplest free-volume treatment of our hard spheres we now expand the point molecules partitioned with single occupancy among the N cells back to elastic spheres of diameter a . The average volume in which a molecule is now free to move is reduced, owing to the average volume occupied by the sphere itself, to $v_f = [v^{\frac{1}{3}} - v_0^{\frac{1}{3}}]^3$ where

$$v_0 = a^3/\sqrt{2} \quad (20)$$

is the minimum (regular close packing) value of v for hard spheres. We can replace Eq. (19) in this approximation by

$$A = -N\beta^{-1} \ln v_f + \text{constant}' \quad (21)$$

with v_f given by Eq. (20). The pressure is obtained from

$$p = - \left(\frac{\partial A}{\partial V} \right)_{N,T} \quad (22)$$

and thus the equation of state^{44,45} is found to be

$$pv\beta - 1 = 1/[(v/v_0)^{\frac{1}{3}} - 1] \quad (23)$$

Clearly Eq. (23) obtained via Eq. (19) is expected to be most applicable at high densities when the system approximates most closely to the idealized solid. We should note that Eq. (23) has no virial development in powers of ρ .

The serious defects of the simplifying approximations made in these lattice theories become apparent because of the failure to obtain significant improvement when attempts are made to remedy their most crude formulations. On the other hand, in rigorous formulations the lattice loses any real intuitive significance and the concomitant mathematical difficulties of the many-body problem are reintroduced.

IV. THE HARD SPHERE SYSTEM

The hard sphere potential φ has the form

$$\varphi = \begin{cases} \infty & \text{if } r < a \\ 0 & \text{if } r > a \end{cases} \quad (24)$$

The derivative of Eq. (24) needed for the equation of state (4) is*

$$d\varphi/dr = -kT \delta(r - a) \quad (25)$$

where $\delta(x)$ is the Dirac delta function of x . When Eq. (25) is substituted into Eq. (4) one finds that

$$\frac{p}{\rho kT} = 1 + \frac{2}{3}\pi\rho a^3 g(a) \quad (26)$$

showing that only $\rho g(a)$, the probability density of having two spheres in contact, rather than the whole function $\rho g(r)$, is necessary to find the equation of state.

* Since

$$\frac{d}{dr} e^{-\varphi(r)/kT} = \delta(r - a + 0) = -\frac{\varphi'(r)}{kT} e^{-\varphi(r)/kT}.$$

Exact results derived for the three-dimensional hard sphere system can often be immediately transcribed to the two- or the one-dimensional hard sphere system from purely dimensional considerations. To do this we must correctly identify in the formulas in which they occur the volume V of the container, the volume element $d\mathbf{r}$, and the density $\rho = N/V$ in three dimensions with the area A of the container, the areal element $d\mathbf{r}$, and the density $\rho = N/A$ in two dimensions and the total lineal length L of the container, twice the lineal element $2dr$, and the density $\rho = N/L$ in one dimension. Thus, e.g., the analogs of (26) are found as soon as the three-dimensional mutual exclusion volume $\frac{2}{3}\pi a^3$ is transcribed, leading to

$$\frac{p}{\rho kT} = 1 + \frac{1}{2}\pi\rho a^2 g(a) \quad (27)$$

for the two-dimensional hard sphere system (spherical discs of diameter a lying on the plane) and

$$\frac{p}{\rho kT} = 1 + \rho a g(a) \quad (28)$$

for the one-dimensional hard sphere system (rigid line segments of length a lying on the straight line).

We are now in a position to apply one of the few known exact existence theorems concerning the partition function Q_N and the phase changes of any fluid. Van Hove⁴⁶ has shown that (using very weak assumptions about the finite-ranged φ) in the limit as $N \rightarrow \infty$, keeping ρ and T fixed:

- (1) $\lim_{N \rightarrow \infty} N^{-1} \ln Q_N$ exists and is a function of ρ and T only* and
- (2) the thermodynamic pressure p is a function of ρ and T only, $p(\rho, T)$, with slope

$$\left[\frac{\partial p}{\partial (1/\rho)} \right]_T \leq 0 \quad (29)$$

* This is the negative value of the configurational Helmholtz free energy per molecule of fluid divided by kT .

In the case of the hard sphere system

$$e^{-\beta\varphi(r)} = \begin{cases} 0 & \text{if } r \leq a \\ 1 & \text{if } r > a \end{cases} \quad (30)$$

by virtue of Eq. (24), and thus $g(a)$, given by Eq. (5) and evaluated at $r_{12} = a$, can only be a function of N , V and a . Combining this with van Hove's demonstration⁴⁶ that p is a function of ρ and T only, one can conclude that the right-hand sides of Eqs. (26)–(28) are dimensionless functions,

$$p/\rho kT = h_n(a^n \rho) \quad (31)$$

of a single variable, the dimensionless reduced density $a^n \rho$ in $n = 1, 2$ and 3 dimensions respectively. The temperature thus enters the classical hard sphere equation of state only as a scaling parameter for the pressure. Equation (31) also serves as a suitable state principle for the comparison of thermodynamic properties of hard sphere fluids of different diameters a .

At a sufficiently low density, the virial expansion [cf. Eq. (7)] of Eq. (31) begins as follows:

$$\frac{p}{\rho kT} - 1 = \begin{cases} b\rho + \frac{5}{8}b^2\rho^2 + 0.2896b^3\rho^3 + (0.115 \pm 0.005)b^4\rho^4 \\ \quad \quad \quad + \dots & \text{(in 3 dim.)} \\ b\rho + 0.782b^2\rho^2 + 0.5327b^3\rho^3 + (0.31 \pm 0.016)b^4\rho^4 \\ \quad \quad \quad + \dots & \text{(in 2 dim.)} \\ b\rho + b^2\rho^2 + b^3\rho^3 + b^4\rho^4 + \dots & \text{(in 1 dim.)} \end{cases} \quad (32)$$

with the second virial coefficient B_2 given by

$$B_2 = b = \begin{cases} 2\pi a^3/3 & \text{(in 3 dim.)} \\ \pi a^2/2 & \text{(in 2 dim.)} \\ a & \text{(in 1 dim.)} \end{cases} \quad (33)$$

The first three virial coefficients are easily computed, the fourth with considerably more effort.^{47–49} The fifth virial coefficients (except for the one-dimensional fluid) are Monte Carlo estimates.^{11,50} Nijboer and van Hove⁵¹ have also expanded $g(r)$ in powers of ρ , up to and including the second power.

With $R = r/a$ they find,⁵¹ $g(R) = 0$ for $R < 1$,

$$g(R) = 1 + \rho g_1(R) + \rho^2 \left\{ \frac{1}{2} [g_1(R)]^2 + \varphi(R) + 2\psi(R) + \frac{1}{2} \chi(R) \right\} + \dots \quad R \geq 1 \quad (34)$$

where

$$g_1(R) = \begin{cases} \frac{2}{3}\pi(2 - \frac{3}{2}R + \frac{1}{8}R^3) & \text{for } R \leq 2 \\ 0 & \text{for } R \geq 2 \end{cases}$$

$$\varphi(R) = \begin{cases} \pi^2[-R^6/1260 + R^4/20 - R^3/6 + R^2/4 + (9/5)R - 9/4 + (27/70)(1/R)] & \text{for } 1 \leq R \leq 3 \\ 0 & \text{for } R \geq 3 \end{cases}$$

$$\psi(R) = \begin{cases} \pi^2[R^6/1260 - R^4/20 + R^3/6 + R^2/4 - (97/60)R + 16/9 - (9/35)(1/R)] & \text{for } 1 \leq R \leq 2 \\ 0 & \text{for } R \geq 2 \end{cases}$$

and

$$\begin{aligned} \chi(R) = & -[g_1(R)]^2 + \pi\{-(3/280)R^4 + (41/420)R^2\}(3 - R^2)^{\frac{1}{2}} \\ & + \pi\{-(23/15)R + (36/35)(1/R)\} \arccos \{R[3(4 - R^2)]^{-\frac{1}{2}}\} \\ & + \pi\{(3/560)R^6 - (1/15)R^4 + \frac{1}{2}R^2 + (2/15)R - (9/35)(1/R)\} \\ & \quad \arccos \{(R^2 + R - 3)[3(4 - R^2)]^{-\frac{1}{2}}\} \\ & + \pi\{(3/560)R^6 - (1/15)R^4 + \frac{1}{2}R^2 - (2/15)R + (9/35)(1/R)\} \\ & \quad \arccos \{(-R^2 + R + 3)[3(4 - R^2)]^{-\frac{1}{2}}\} \end{aligned}$$

for $1 \leq R \leq \sqrt{3}$;

$$\begin{aligned} \chi(R) &= -[g_1(R)]^2 & \text{for } \sqrt{3} \leq R \leq 2 \\ \chi(R) &= 0 & \text{for } R \geq 2 \end{aligned}$$

For a real fluid at sufficiently high temperatures the slope $[\partial p / \partial (1/\rho)]_T$ is positive for all values of ρ , in accordance with Eq. (29). At lower temperatures, there can be one or more regions in which $[\partial p / \partial (1/\rho)]_T = 0$. These flat portions of the curve in the (p, ρ^{-1}) phase diagram possess mathematical singularities at both ends as a consequence of the limiting process $V, N \rightarrow \infty$ with ρ, T constant under which we are studying the fluid.^{9,10} The flat portion corresponds to a two-phase coexistence region.

The familiar S-shaped loop which is found for the van der Waals equation of state cannot be obtained in this limit by virtue of van Hove's⁴⁶ result, Eq. (29). We have to be careful, of course, to make sure that our potential has only a finite range and satisfies otherwise the conditions under which this theorem can be demonstrated. For a system with N finite we do not expect, in general, any singularities in either Q_N or p as functions of ρ^{-1} . If a van der Waals loop occurs in the phase diagram of such a finite system one can attempt to identify the flat two-phase portion of the actual thermodynamic system (for which $N, V \rightarrow \infty$) by applying Maxwell's theorem of "equal areas". Needless to say, in any specific case in which we do this we must be able subsequently to demonstrate the validity of this procedure. These considerations possess particular bearing on the two- and three-dimensional hard sphere fluid. Since we cannot study the phase diagram experimentally and we do not have a satisfactory analytical theory of the phase transition for these systems we must infer the phase behavior from machine computed simulations of this behavior by a finite and relatively small number (as compared to Avogadro's number) of hard spheres.

The molecular dynamic computations carried out by Alder and Wainwright¹ deal in three dimensions with 32 to 500 hard spheres located in a rectangular box,¹ and in two dimensions with up to 870 hard circular discs.⁵² The position and velocity of each particle is stored in the memory of the calculating machine and the changes in time of these entities is obtained by the numerical solution of Newton's equations. Clearly, because of the nature of the hard sphere intermolecular force, the entire dynamic calculation reduces to a succession of two-body collisions. A printed record is obtained of the number of collisions as a function of time and also the sum of the absolute values of the momentum changes. The velocity changes are recorded on magnetic tape. From these the pressure is calculated from the growth rate of the momentum sum Σ using the virial theorem (cf. Section II). If $\mathbf{r}_{a_i}$ and $\mathbf{r}_{b_i}$ are the positions of particles a and b involved in the i th collision, and $\Delta\mathbf{v}_{a_i}$ is the change in velocity of particle a in this collision ($\Delta\mathbf{v}_{a_i} = -\Delta\mathbf{v}_{b_i}$) then

$$\Sigma = \sum_i (\mathbf{r}_{a_i} - \mathbf{r}_{b_i}) \cdot \Delta\mathbf{v}_{a_i} \quad (35)$$

and

$$\frac{p}{\rho k T} - 1 = -\frac{1}{N \overline{C^2}} \frac{\Delta \Sigma}{\Delta t} \quad (36)$$

where N is the number of particles in the system and $\overline{C^2}$ is the mean square velocity relative to the center of mass of the system.

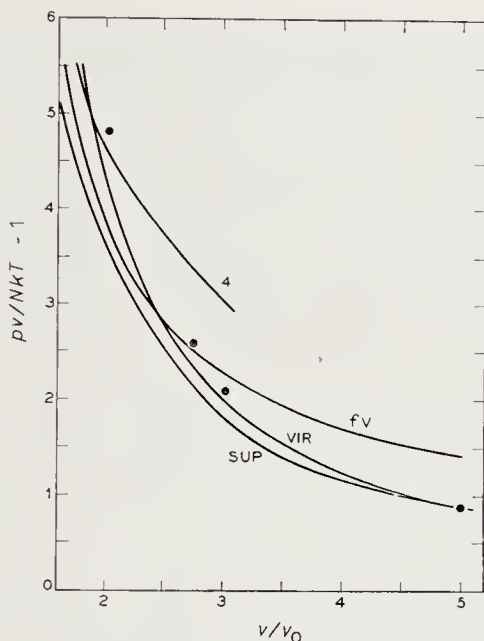


Fig. 1. Equation of state in the low density region. SUP—superposition theory, VIR—five-term virial expansion, fv—free-volume theory, 4—four particle results; the dots refer to the machine calculations for systems with 32 or more particles.

Periodic boundary conditions are imposed at the walls of the rectangular box enclosing the particles. Thus, a particle which passes out through one side of the box reenters with the same velocity through the opposite side. Initially, in most runs, the particles are periodically arranged in a close-packed structure, which, depending on the number of particles studied and the geometry of the box, could be either face-centered cubic or close-packed hexagonal. In general, all particles are started with equal kinetic energies but velocities in random directions. The velocity distribution equilibrates monotonically in about 2–4 collisions per particle.

The numerical results obtained¹ for the equation of state of the three-dimensional hard sphere system in the low density region are shown in Fig. 1. A comparison is made with the equation of state obtained by numerical integration of Eq. (13) subject to Eq. (15), the "superposition theory" [cf. Eq. (11)], the free-volume equation of state (23), and the five-term virial expansion (32). The last

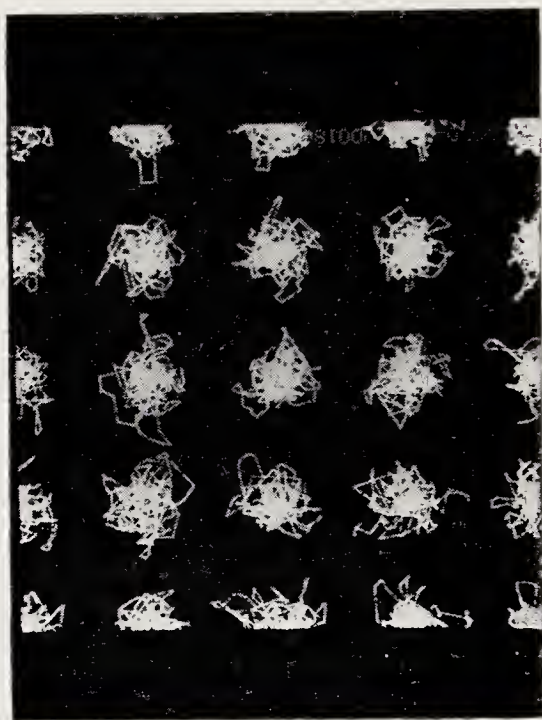


Fig. 2. 3000 collisions in the middle of the initial "solid" region.

clearly gives the best fit, while the free-volume theory appears to be wholly inadequate in this density region.

At intermediate densities, $1.5 \leq v/v_0 \leq 1.8$, there exists a much more complex two-state behavior of the system. This is of considerable interest in view of the indication from the numerical solution of the superposition theory of a phase transition at or near $v/v_0 \simeq 1.5$. In the intermediate density region the systems exhibit tendencies to undergo spontaneous transitions between states of considerably different pressures. Thus, for all systems in this density region which start out in a face-centered-cubic configuration the pressure remains steady at a low value for a

variable period of time and then suddenly jumps to a higher value. After staying at the higher pressure value the system spontaneously goes back to the lower pressure state before returning to the high pressure state. A cathode ray oscilloscope attached to the calculating machine was used to make traces in a plane projection of the positions of the centers of the particles. Figures 2 and 3 show

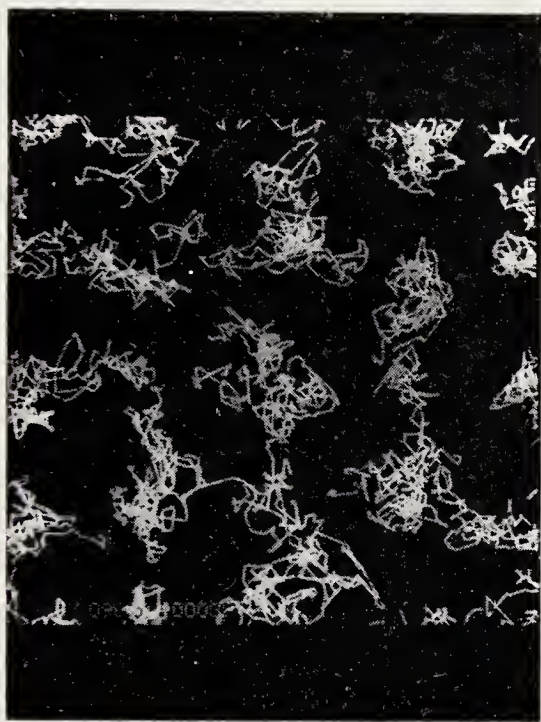


Fig. 3. 3000 collisions in the middle of the "fluid" (high pressure) region.

the traces made by 3000 collisions of the centers of 32 particles at $v/v_0 = 1.525$ in the initial low pressure state and in the subsequent high pressure state. In the first picture the particles centers are essentially localized about the sites of the projected lattice; thus the low pressure state corresponds to a "solid" while the high pressure state, with its wandering particle centers, corresponds to a "fluid". The edges in this figure are due to the use of the periodic boundary condition. Figure 4 summarizes the equation of state behavior of these systems in the intermediate density region, showing both the "solid" and "fluid" branches.

Alder and Wainwright¹ argue that in these small systems it is not possible to have both the "solid" and "fluid" together in equilibrium, but the whole system is either in one state or another. The phase space of the system consists presumably of two regions, corresponding to the high pressure and low pressure states, connected by only a very narrow passage (for a finite number of

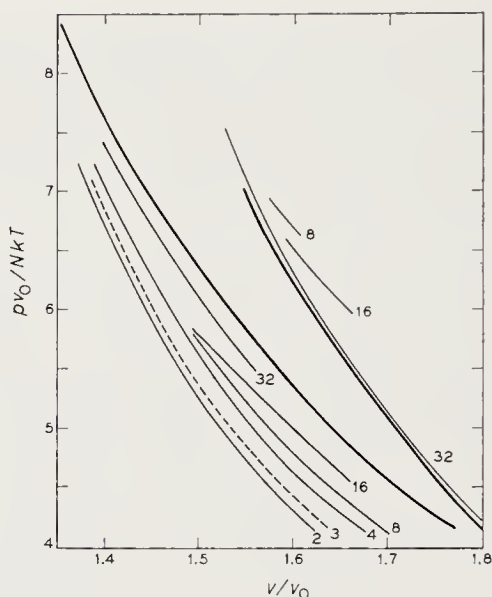


Fig. 4. Equation of state in the transition region showing both "fluid" and "solid" branches. The curves are labeled by the number of particles studied. Heavy lines refer to systems containing 96 or more particles.

particles). To clarify some of these ambiguities Alder and Wainwright⁵² studied the behavior of the analogous two-dimensional hard disc system. By doing this an effectively much larger system (up to 870 particles) could be handled by the capacity of the computer and the lattice of the nearly close-packed phase is uniquely defined. The results obtained for the equation of state are summarized in Fig. 5. The smaller systems, like the 72 hard discs system whose behavior is shown in this figure by the triangular points, behave like the analogous three-dimensional systems of relatively few particles. They exhibit two distinct branches corresponding to the high and low pressure branches of Fig. 4. The system of 870 hard discs, on the other hand, exhibited a

typical van der Waals like loop. Apparently, the two "phases" can exist here side by side. This is confirmed by the cathode ray pictures. The density change across the transition is about 4% and the corresponding entropy change is small ($\Delta S/Nk \simeq 0.36$).

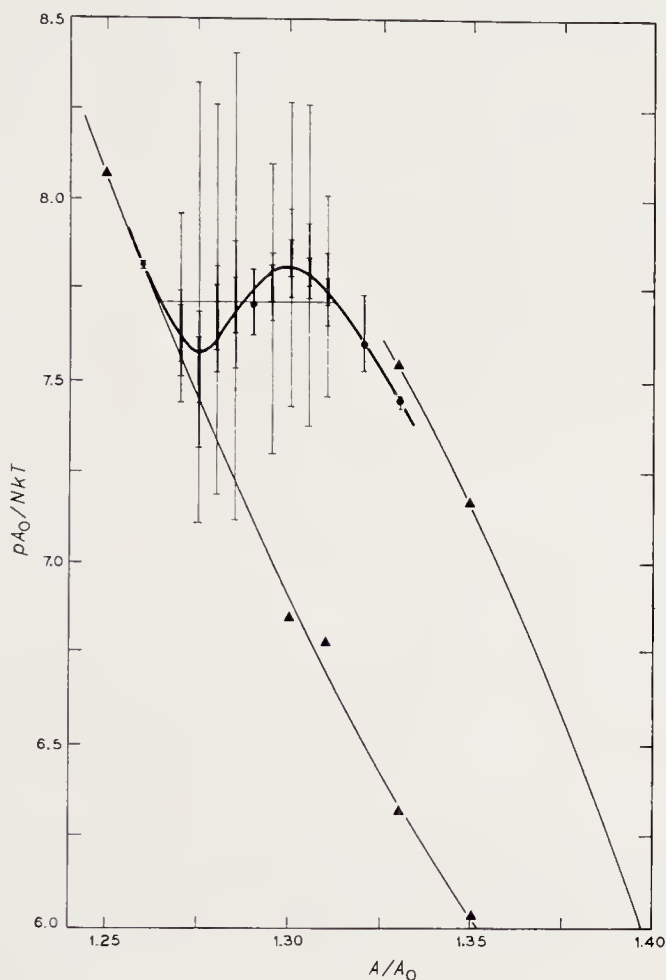


Fig. 5. The equation of state of 870 hard discs in the phase transition region. A_0 is the area of the system at close packing. The triangles refer to points for 72 particles.

This corresponds to a very much smaller communal entropy change (0.06) across the transition than is to be expected if the difference between a dense fluid and a solid is one of accessibility of all the volume in the fluid and localization of a molecule to the "free volume" of a cell in the solid. This strongly suggests the

existence of a first-order phase transition. The extrapolation of the isotherm shape from a system of a finite number of particles to one for which $N \rightarrow \infty$ may yield, besides an isotherm with a flat portion (indicated by the Maxwell construction in Fig. 5), an isotherm in which this region has shrunk to a point (horizontal inflection point) or even an isotherm in which only the slope changes discontinuously at a point but $[\partial p / \partial (1/\rho)]_T \neq 0$ for any density. The last two possibilities must still be excluded by theoretical

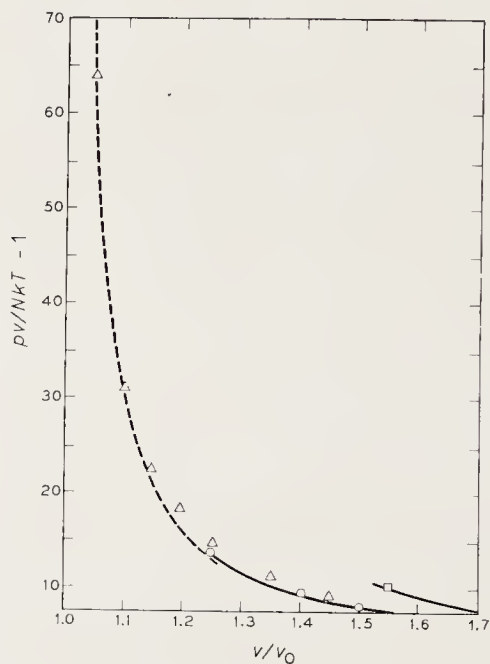


Fig. 6. Equation of state in the high density region. The solid line represents the data for the 32 hard sphere system in the "solid" and "fluid" branches. The dashed line is calculated by the free-volume theory, Eq. (23).

considerations before we can come to definite conclusions about the phase diagram of the system. The high density region on the "solid" branch of a three-dimensional hard sphere system is shown in Fig. 6. As can be seen from the graph, the free-volume theory, cf. Eq. (23), appears to be quite accurate in this density region for this branch of the isotherm. The molecular dynamic computations of Alder and Wainwright^{1,52} are not restricted, like the Monte Carlo calculations, to the computation of equilibrium

properties only. These authors¹ have also studied for this system the approach of the molecular distribution function to its equilibrium value, the Boltzmann H function, the velocity autocorrelation function and the transport coefficients.

The Monte Carlo method for obtaining the equation of state of interacting molecules was devised by Metropolis *et al.*⁵³ and has been applied to both the hard sphere^{2,50,54} and the Lennard-Jones fluid.⁵⁵ In order to make use of a discrete stochastic process one first subdivides the $3N$ dimensional configuration space of a system of $3N$ molecules, confined to a volume V at temperature T , into a sufficiently large number S of cells. The positions of the N molecules are specified by giving the single number associated with the cell into which the representative $3N$ dimensional point describing the location of the N molecules falls. The method then consists^{53,55} in generating a Markov chain with constant transition probabilities⁵⁶ in which the states of the chain are the points (or cell numbers) in the $3N$ dimensional configuration space. To each cell, associated with some integer k , $k = 1, 2, \dots, S$, there corresponds a state of the Markov chain, as well as other variables such as U_k , the total potential energy of configuration k [cf. Eq. (1)], etc. The object of the Monte Carlo method is to generate a Markov chain in which asymptotically each state k recurs with a frequency proportional to the Boltzmann factor $\exp(-U_k/kT)$ for that state. The average over the chain of any function of the configuration state, such as U_k , in which each occurrence of any state is given equal weight, will converge^{53,55} to the corresponding petite canonical ensemble average⁶ of the same quantity as the chain length increases. This can be accomplished⁵⁵ by choosing some set (there is no unique set) of transition probabilities from state j to state k , p_{jk} , with j and k in the same ergodic class, which are normalized

$$\sum_{k=1}^S p_{jk} = 1 \quad (j = 1, 2, \dots, S) \quad (37)$$

and satisfy the condition of microscopic reversibility

$$\exp(-U_j/kT)p_{jk} = \exp(-U_k/kT)p_{kj} \quad (38)$$

for all j, k . Explicit examples of the p_{jk} are given in References 50, 53 and 55.

The calculating machine generates the chain of configurations, again using periodic boundary conditions, subject to the transition probabilities p_{jk} , satisfying Eqs. (37) and (38), by moving successively one of the N molecules "selected at random, but uniformly, by a random but uniform amount".⁵⁵ The pressure is obtained by

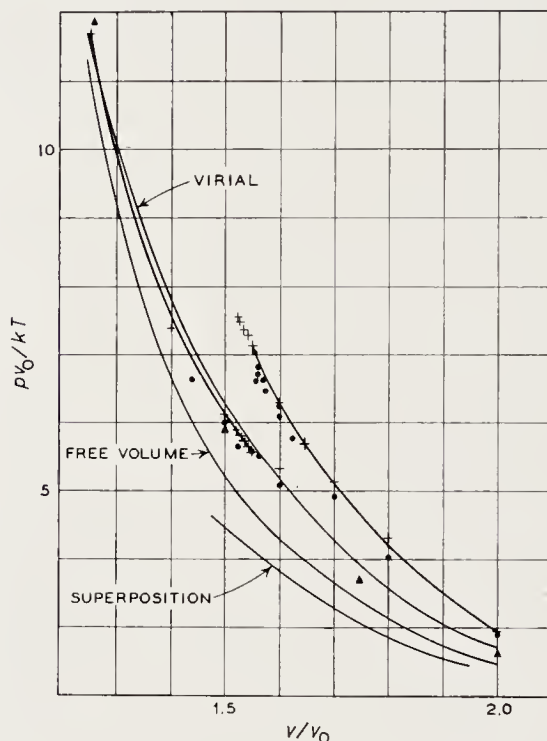


Fig. 7. Equation of state of hard spheres. The heavy solid line represents Alder and Wainwright's¹ 108 molecule results; crosses their 32 molecule results; black circles and triangles Monte Carlo results for 32 molecules given in References 54 and 50, respectively.

the Markov chain average of the virial $\frac{1}{2}\Sigma' r_{ij} d\varphi(r_{ij})/dr_{ij}$. The initial configuration is, in general, taken to be a regular face-centered cubic lattice arrangement.

The resulting⁵⁴ equation of state for 32 three-dimensional hard spheres is shown in Fig. 7. One sees again the two-branched transition behavior already noted by Alder and Wainwright.¹ The numerical agreement between the isotherms shown in Fig. 7, computed by such different methods, is gratifying and lends mutual credibility to these computations.

V. THE EQUATION OF STATE OF THE HARD SPHERE FLUID

The scaled particle theory of fluids developed by Reiss, Lebowitz, Helfand and Frisch^{3,4,39-41} need concern itself [in the case of hard spheres by virtue of Eq. (26)] only with calculating $g(a)$. To accomplish this we focus our attention on a spherical cavity of radius at least r centered about a fixed point in the fluid. A cavity is defined as a region of space devoid of molecular (hard sphere) centers (see Fig. 8). Such a cavity can be formed spontaneously in our fluid as a result of a local density fluctuation.

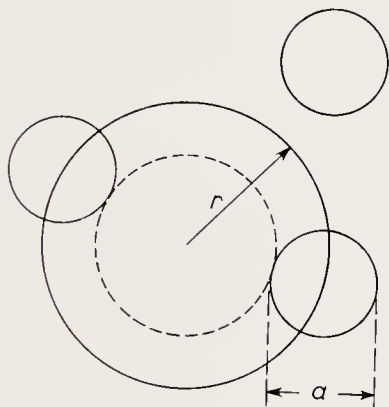


Fig. 8. A spherical cavity of radius r in a hard sphere fluid.

We denote by $p_0(r)$ the probability of finding a spherical cavity of radius *at least* r centered on an arbitrary fixed point $\mathbf{R}$ in our fluid. The negative rate of change of p_0 , $-(dp_0/dr) dr$, is the probability of finding a cavity whose radius lies between r and $r + dr$.^{*} This probability is in turn equal to the product of the probability of finding a spherical cavity of radius at least r , $p_0(r)$, and the conditional probability that there is a center of some molecule between r and $r + dr$ when there is no center inside the sphere of radius r . We call this conditional probability $\rho G(r, \rho, a) 4\pi r^2 dr$. Note that $\rho G(r, \rho, a) = \rho G(r)$ is a conditional probability density[†]

* The negative sign clearly follows, since the probability of finding a cavity of radius at least r decreases as r increases.

† Since when multiplied by the spherical volume element $dv = 4\pi r^2 dr$ it yields the conditional probability.

which can alternatively be thought of as the average density of hard sphere centers in contact with the boundary of our spherical cavity.³ Thus

$$-\frac{d\phi_0}{dr}dr = \phi_0(r) \cdot \rho G(r) 4\pi r^2 dr$$

or

$$-\frac{1}{4\pi r^2} \frac{d \ln \phi_0(r)}{dr} = \rho G(r) = -\frac{d \ln \phi_0}{dv} \quad (39)$$

$$dv = 4\pi r^2 dr$$

The significance of $G(r)$ arises from the fact, seen from Fig. 9, that a fixed spherical cavity of radius a affects the remainder of

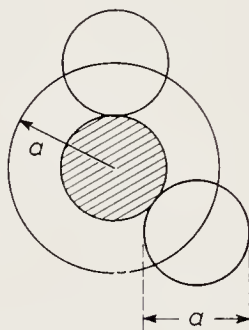


Fig. 9. A spherical cavity of radius a . (The diameter of the spherical shaded region is a .)

the fluid precisely like another hard sphere molecule fixed at the center of the cavity. We have, in particular,³

$$G(a) = g(a) \quad (40)$$

More generally, a spherical cavity of radius $r = (a + b)/2$ acts like a fixed solute hard sphere of diameter b in the remaining (solvent) hard sphere molecules each of diameter a . The equations of state of the three-, two- and one-dimensional hard sphere fluids can be written in terms of the appropriate G as [cf. Eqs. (26)–(28)]

$$\frac{p}{\rho k T} - 1 = \begin{cases} \frac{2}{3}\pi\rho a^3 G(a) & (\text{in 3 dim.}) \\ \frac{1}{2}\pi\rho a^2 G(a) & (\text{in 2 dim.}) \\ \rho a G(a) & (\text{in 1 dim.}) \end{cases} \quad (41)$$

We shall now use (39) to study $G(r)$ in order to find the desired value of $G(a)$. Note that (39) is also correct in two or one dimensions if the appropriate volume element dv is used [$dv = 2\pi r dr$ (2 dim.) and $dv = 2 dr$ (1 dim.)]. To express $G(r)$ in terms of physical entities we introduce the reversible work, i.e., free energy, needed to form a spherical cavity of radius r , $W(r)$. By a general principle in classical statistical mechanics the probability of the spontaneous occurrence of some specified situation is equal to the negative exponential of the reversible work necessary to create the situation divided by kT .* Thus, in particular,

$$p_0(r) = e^{-W(r)/kT} \quad (42)$$

Now the work required to increase the radius of the cavity from r to $r + dr$, dW , can be written as a contribution proportional to the volume change dv , whose coefficient is the pressure of the fluid p plus a contribution proportional to the change in surface area dS (equal to $8\pi r dr$ in three dimensions and $2\pi dr$ in two dimensions), whose coefficient is a surface free energy, i.e., a surface tension σ , viz.

$$dW(r) = p dv + \sigma dS = kT\rho G(r) dv \quad (43)$$

by virtue of (39) and (42). The surface tension σ refers to the surface tension of hard sphere molecules against a rigid wall (since a cavity acts like a rigid wall) and will in general be a function of the curvature $2/r$ and thus r , $\sigma = \sigma(r)$.

From (43), on dividing by dv , we find the desired expression for $G(r)$,

$$G(r) = \frac{p}{\rho kT} + \frac{\sigma(r)}{\rho kT 2r} \quad (44)$$

in terms of purely physical entities. As is well known, the surface tension σ attains a constant value,⁹⁻¹¹ $\sigma(r) \rightarrow \sigma_0$, at a plane wall, $r \rightarrow \infty$. Thus taking the limit as $r \rightarrow \infty$ of (44) we find that

$$G(\infty) = \frac{p}{\rho kT} = 1 + \begin{cases} \frac{2}{3}\pi\rho a^3 G(a) & (3 \text{ dim.}) \\ \frac{1}{2}\pi\rho a^2 G(a) & (2 \text{ dim.}) \\ \rho a G(a) & (1 \text{ dim.}) \end{cases} \quad (45)$$

* A thorough discussion of this fluctuation theorem in a context similar to the one for which we apply this theorem can be found in R. C. Tolman, *The Principles of Statistical Mechanics*, Oxford University Press, London, 1938; Sec. 141.

As can be seen from (43), the result (45) could also be derived by considering the normal stress at the surface of the cavity, which is by definition dW/dv . This normal stress is purely kinetic and is thus equal to kT times the density of molecular centers at the surface of the cavity $\rho G(r)$. As the cavity becomes very large, the surface of the cavity approaches a plane and the normal stress becomes equal to p ,

$$p = \left. \frac{dW}{dv} \right|_{r \rightarrow \infty} = \rho k T G(\infty) \quad (46)$$

Equation (45) already suffices to specify exactly the equation of state of a one-dimensional hard sphere fluid. To see this we note that in one dimension (see Fig. 10) no two molecules lying

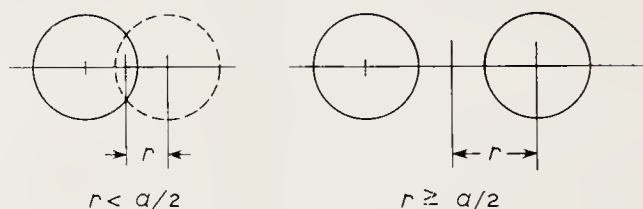


Fig. 10. Cavities in a one-dimensional hard sphere fluid.

on opposite sides of a cavity of radius $r > a/2$ can ever interact (across the cavity), i.e., molecules cannot “tell” what size cavity they are next to for $r > a/2$. Thus $G(r)$ must be independent of r for $r > a/2$ and as a special case the molecule-molecule contact density $\rho G(a)$ must be equal to the molecule-wall density $\rho G(\infty)$,

$$G(a) = G(\infty) \quad (46a)$$

Introducing (46a) into (45) immediately gives us then the well known Tonks’ equation of state⁴⁴

$$\frac{p}{\rho k T} = \frac{1}{1 - \rho a} \quad (47)$$

which reminds one of the one-dimensional analog of van der Waals equation. The reason that the one-dimensional case is so simple compared with the higher dimensional ones is that there is no surface work contribution since there is no "surface" in one dimension. Indeed we can write

$$dW = p(2 dr) = p dv \quad \text{for } r > a/2 \quad (48)$$

In two or more dimensions we need to know much more about $G(r)$ before we can find the equation of state, since we must elucidate the nature of the surface tension $\sigma(r)$ in (44.) We proceed by considering again $p_0(r)$, the probability of having no molecular centers inside our cavity. This is clearly equal to the probability of *all* molecular centers being *outside* the cavity, and thus by virtue of (2) and (3)

$$p_0(r) = \int_{V - \omega(\mathbf{R})}^{(N)} \exp \left[-\frac{1}{2kT} \sum_i \sum_j \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N / Q_N \quad (49)$$

where $V - \omega(\mathbf{R}, r)$ is the volume of the container exclusive of a sphere of radius r about the point $\mathbf{R}$, $\omega(\mathbf{R}, r)$. By introducing the Heaviside function $\varepsilon(\mathbf{r}_i) = \varepsilon(\mathbf{r}_i; \mathbf{R}, r)$ where

$$\varepsilon(\mathbf{r}_i) = \begin{cases} 1 & \text{if } |\mathbf{r}_i - \mathbf{R}| < r \\ 0 & \text{if } |\mathbf{r}_i - \mathbf{R}| > r \end{cases} \quad (50)$$

we can rewrite (49) with integrals extending over the volume of the container, viz.,

$$p_0(r) = \int \dots \int_V^{(N)} \prod_{i=1}^N [1 - \varepsilon(\mathbf{r}_i)] \exp \left[-\frac{1}{2kT} \sum_{i \neq j} \varphi(\mathbf{r}_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N / Q_N \quad (51)$$

Expanding the product of $(1 - \varepsilon)$ factors into a sum of products of ε factors,

$$\begin{aligned}
 \prod_{i=1}^N [1 - \varepsilon(\mathbf{r}_i)] &= 1 - \sum_{i=1}^N \varepsilon(\mathbf{r}_i) + \frac{1}{2} \sum_i \sum_j \varepsilon(\mathbf{r}_i) \varepsilon(\mathbf{r}_j) - \dots, \text{ etc.} \\
 p_0(r) &= \frac{Z_N}{Z_N} \\
 &- \int \dots \int \sum_{i=1}^N \varepsilon(\mathbf{r}_i) \exp \left[-\frac{1}{2kT} \sum \sum \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N / Q_N \\
 &+ \frac{1}{2} \int \dots \int \sum \sum \varepsilon(\mathbf{r}_1) \varepsilon(\mathbf{r}_j) \exp \left[-\frac{1}{2kT} \sum \sum \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N / Q_N \\
 &- \dots = 1 \\
 &- \frac{N \int \varepsilon(\mathbf{r}_1) d\mathbf{r}_1 \int \dots \int \exp \left[-\frac{1}{2kT} \sum \sum \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N}{V \int \dots \int \exp \left[-\frac{1}{2kT} \sum \sum \varphi(r_{ij}) \right] d\mathbf{r}_1 \dots d\mathbf{r}_N} \\
 &+ \dots = 1 - \frac{4}{3} \pi r^3 \rho + \frac{1}{2} \int \int \rho^2 g(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 - \dots = 1 - \sum_{n=1} (-1)^n F_n
 \end{aligned} \tag{51a}$$

with

$$\begin{aligned}
 F_1 &= \frac{4}{3} \pi r^3 \rho \\
 F_2 &= \frac{1}{2} \int \int \rho^2 g(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 \\
 F_n &= \frac{\rho^n}{n!} \int \dots \int g_n(\mathbf{r}_1, \dots, \mathbf{r}_n) d\mathbf{r}_1 \dots d\mathbf{r}_n
 \end{aligned} \tag{52}$$

where the F_n are the average number of n tuple (hard sphere centers) in the spherical region of radius r . This is particularly easily seen for F_1 since it is just the product of the volume of the region, $\omega(\mathbf{R}, r) = \frac{4}{3} \pi r^3$, times the average density of molecular centers, ρ . Equation (51) incidentally is the hard sphere analog of the Mayer-Montroll series.⁵⁷

Consider a cavity for which $r < a/2$. Clearly no more than one particle center can lie in such a cavity and thus $F_2 = F_3 = \dots = F_n = \dots = 0$,

$$p_0(r) = 1 - \frac{4}{3}\pi r^3 \rho \quad (r < a/2) \quad (53)$$

and using (24)

$$G(r) = -\frac{1}{4\pi r^2 \rho} \frac{d \ln p_0(r)}{dr} = \frac{1}{1 - \frac{4}{3}\pi r^3 \rho} \quad (r < a/2) \quad (54)$$

For $a/2 \leq r < a/\sqrt{3}$ two particle centers can lie in the cavity,

$$p_0(r) = 1 - F_1 + F_2 \quad (a/2 \leq r < a/\sqrt{3}, \text{ etc.}) \quad (55)$$

till finally at $r = a + 0$ twelve particle centers* can be accommodated. From Eq. (55) we can verify directly by differentiation that $G(r)$ and $(\partial G/\partial r)$ are continuous at $r = a/2$. The first discontinuity which occurs at $r = a/2 + 0$ is in the second derivative $\partial^2 G/\partial r^2$; it is proportional to $G(a)$ since another hard sphere center can just be accommodated at $a/2 + 0$, and the discontinuities at $r = a/\sqrt{3} + 0$, etc., occur in higher and higher derivatives. Thus, we are dealing with a very smooth function $G(r)$ (its first derivative is everywhere continuous in $a/2 \leq r \leq a$) whose exact value is given by Eq. (54) up to $r = a/2$. Unfortunately, it becomes prohibitively difficult to study $G(r)$ by a continuation of the above process. We thus resort to an approximation. We shall approximate the exact $G(r)$, which is not analytic but smooth, by an analytic function in $a/2 \leq r < \infty$ which is the analytic solution of certain exact integral equations satisfied also by the correct $G(r)$.

The first of these exact integral equations is derived by noting that a spherical cavity of radius a behaves exactly like another fixed hard sphere molecule. The reversible work needed to add such a fixed hard sphere is just $W(a)$

$$W(a) = kT \int_0^{v(r=a)} \rho G(r) dv = 4kT\pi\rho \int_0^a G(r)r^2 dr \quad (3 \text{ dim.}) \quad (56)$$

the reversible work of forming a cavity of radius a . Thus the chemical potential μ_a of another (added, nonfixed) hard sphere

* Actually to find $g(a)$ one need know nothing about F_n for $n \geq 10$ (3 dim.) or $n \geq 5$ (2 dim.).

molecule can be obtained by adding a contribution due to the free translational motion of the center of mass of the molecule to $W(a)$, viz.,

$$\mu_a = kT \ln \rho_a \Lambda^n + W(a) \quad (57)$$

where $kT \ln \rho_a \Lambda^n$ is the usual free energy per point particle due to translational motion in n dimensions ($n = 1, 2, 3$), $\rho_a = \rho$, the number density, and Λ is the mean thermal de Broglie wavelength of our molecules. More generally, we can obtain the chemical potential of an added hard sphere solute of diameter b in a great excess of our hard sphere fluid, μ_b , by replacing a wherever it occurs in Eq. (57) by b . The first of our desired integral equations is then immediately found³ as a consequence of the well known thermodynamic identity,

$$\frac{\partial p}{\partial \rho} = \rho \left(\frac{\partial \mu_a}{\partial \rho} \right)_T \quad \text{or} \quad p = \int_0^\rho \rho' \left(\frac{\partial \mu_a}{\partial \rho'} \right)_T d\rho' \quad (58)$$

together with Eqs. (41) and (57). The resulting integral equation

$$\frac{2}{3}\pi a^3 \rho^2 G(a, \rho) = \rho^2 \int_0^a 4\pi r^2 G(r, \rho) dr - \int_0^\rho \rho' d\rho' \int_0^a 4\pi r^2 G(r, \rho') dr \quad (59)$$

unfortunately possesses the disadvantage that the variable r is bound and is thus not able to specify uniquely the functional form of G or its desired analytic approximation.

The second exact integral equation can be derived by considering the addition of a hard sphere solute of diameter b to a large excess of our fluid.³ It is an immediate consequence of the thermodynamic identity

$$\left(\frac{\partial p}{\partial \rho_b} \right)_{\rho_a} = \rho_b \left(\frac{\partial \mu_b}{\partial \rho_b} \right)_{\rho_a} + \rho_a \left(\frac{\partial \mu_b}{\partial \rho_a} \right)_{\rho_b} \quad (60)$$

which now replaces Eq. (58). After some manipulation, Eq. (60) yields an inhomogeneous integral equation

$$Q(r, \rho) = -\rho \frac{\partial}{\partial \rho} \left\{ \rho \int_0^r 4\pi r'^2 G(r', \rho) dr' \right\} + \frac{4}{3}\pi \rho r^3 G(r, \rho) \quad (61)$$

with $r = (a + b)/2$ (b being variable), where $Q(r, \rho)$ is the inhomogeneous function defined by

$$Q(r, \rho) = -\frac{2}{3}\pi a^3 \rho \left[\frac{\partial G(a, \rho)}{\partial \rho_b} \right]_{\rho_b \rightarrow 0} \quad (62)$$

Unfortunately, it is not known. Still, using the continuity of G and $\partial G/\partial r$ at $r = a/2 + 0$ one can show that³

$$\lim_{r \rightarrow a/2 + 0} Q(r, \rho) = -(\text{function of } \rho \text{ only})(r - a/2)^2 \quad (63)$$

while for $r \rightarrow \infty$ the dominant term in Q is

$$Q_{\text{dominant}} = -(\text{function of } \rho \text{ only})r^3 \quad (64)$$

Thus, if G is approximated by an analytic function in $a/2 \leq r < \infty$ then by virtue of Eq. (61) so is Q (for a suitable domain of ρ values) and this function can be expanded in a Laurent series. Only a term quadratic in $(r - a/2)$ and cubic in $(r - a/2)$ need be retained in this expansion if Eqs. (63) and (64) are to be satisfied. Introducing this approximate Q into Eq. (61) and solving for the suitable approximate G one finds that

$$G(r, \rho) \approx A(\rho) + \frac{B(\rho)}{r} + \frac{C(\rho)}{r^2} \quad (65)$$

where A , B and C are functions of ρ only.

This functional form of G is not unexpected. Macroscopic thermodynamic considerations by Tolman,⁵⁸ among others,⁵⁹⁻⁶¹ suggest that the surface tension $\sigma(r)$ can be approximated

$$\sigma(r) \approx \sigma_0(\rho) \left[1 - \frac{2}{r} \delta(\rho) a \right] \quad (66)$$

which when substituted into Eq. (44) yields an approximate G ,

$$G(r, \rho) \approx \frac{p}{\rho k T} + \frac{\sigma_0(\rho)}{\rho k T 2r} - \frac{\sigma_0(\rho) \delta(\rho) a}{\rho k T r^2} \quad (67)$$

of the same functional form as Eq. (65).^{*} The significance of $\sigma_0(\rho)$ is that it is the surface tension of a hard sphere fluid against a plane rigid wall, while $\delta(\rho)$ is like the distance between the dividing surface for which the superficial density of matter vanishes and the Gibbs surface of tension of the fluid. The three functions of the

* $p/\rho k T$ for a hard sphere fluid is a function of ρ only, cf. Eq. (31).

density ρ occurring in Eq. (67) or (65) can be found immediately using the known form of G up to $r = a/2$, its continuity and that of its derivative $\partial G/\partial r$ at $r = a/2 + 0$ and either Eq. (45) or the integral equation (59). The fact that both Eqs. (45) and (59) lead to the same coefficients A, B, C lends extra support to the internal consistency of our approximation.

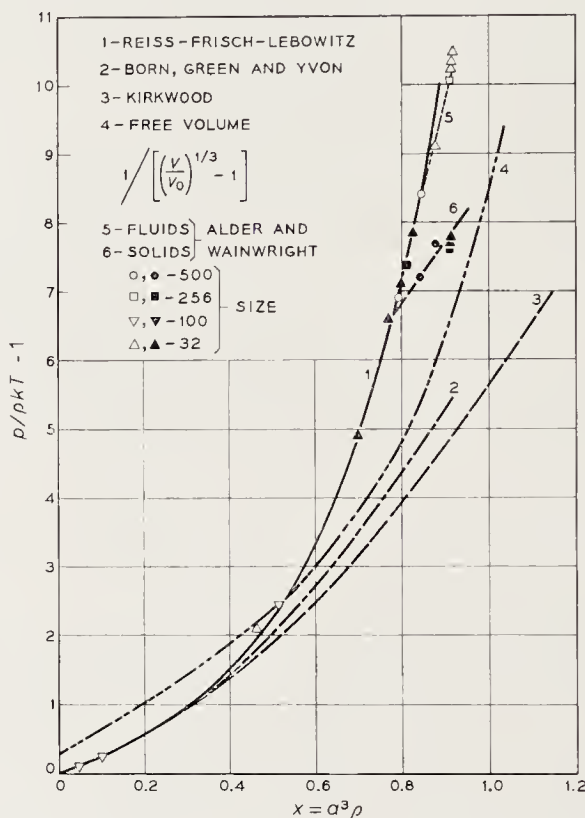


Fig. 11. Comparison of theoretical equations of state with the machine computations of Alder and Wainwright.¹ The line 6 is freely drawn through the machine computed points¹ for the beginning of the "solid" branch and has no theoretical justification. The data for curves 2 and 3 are taken from Kirkwood, J. G., Maun, E. K. and Alder, B. J., *J. Chem. Phys.* **18**, 1040 (1950).

Summarizing, we find that the approximate equation of state obtained from Eq. (67) is (in three dimensions)³

$$G(\infty, \rho) = \frac{p}{\rho k T} = (1 + y_3 + y_3^2)/(1 - y_3)^3 \quad (68)$$

with $y_3 = \pi\rho a^3/6$ and

$$\begin{aligned}\sigma_0(\rho) &= -\left(\frac{kT\pi a^4\rho^2}{8}\right)\left[\frac{1+y_3}{(1-y_3)^3}\right] \\ \delta(\rho) &= \frac{1}{4} - \frac{1}{4}\left(\frac{1-y_3}{1+y_3}\right)\end{aligned}\quad (69)$$

The approximate equation of state is in remarkable agreement with the machine calculations of Wood and Jacobson and Alder and Wainwright, as can be seen from Fig. 11. The virial development of Eq. (68) [cf. Eq. (7)] yields

$$p/\rho kT = 1 + 4y_3 + 10y_3^2 + 19y_3^3 + 31y_3^4 + \dots \quad (70)$$

which compares favorably with the exact virial series

$$p/\rho kT = 1 + 4y_3 + 10y_3^2 + 18.36y_3^3 + (28.3 \pm 1.3)y_3^4 + \dots \quad (71)$$

in that the first three coefficients are exact, the fourth is in error by 3% while the fifth lies within 5% of the uncertainty in our knowledge of that coefficient.

The procedure for finding the approximate equation of state of the two-dimensional hard sphere fluid follows almost step by step that outlined above for the three-dimensional fluid except that the curvature term in Eq. (67) can be neglected.⁴¹ Without entering into further details of the calculations we merely quote the result

$$p/\rho kT = 1/(1-y_2)^2 \quad (72)$$

with $y_2 = \pi\rho a^2/4$. Figure 12 shows that Eq. (72) agrees well with the machine calculation of the previously cited authors.^{1,2,52,62,63} The virial development of Eq. (72) gives

$$p/\rho kT = 1 + 2y_2 + 3y_2^2 + 4y_2^3 + 5y_2^4 + \dots \quad (73)$$

as compared with the exact virial series

$$p/\rho kT = 1 + 2y_2 + 3.128y_2^2 + 4.262y_2^3 + (4.95 \pm 0.25)y_2^4 + \dots \quad (74)$$

In view of the fact that to obtain Eq. (68) or (72) we had to approximate $G(r)$ by an analytic function, we cannot expect these equations to give any indications of a phase transition such as suggested by the machine calculations. Indeed, both of the approximate equations of state do not even diverge at the close-packed densities of $y_3 = 0.740$ and $y_2 = 0.907$, but do for y_3, y_2

$= 1$, which corresponds to the close packing of three-dimensional hard squares of the same area as discs. The non-analytic portions of G , from which phase transitions can mathematically stem, have so far been completely neglected. We have not been able to make further use of some exact known properties of $G(r)$ such as, e.g., the value of the discontinuity in its second derivative at $r = a/2 + 0$.

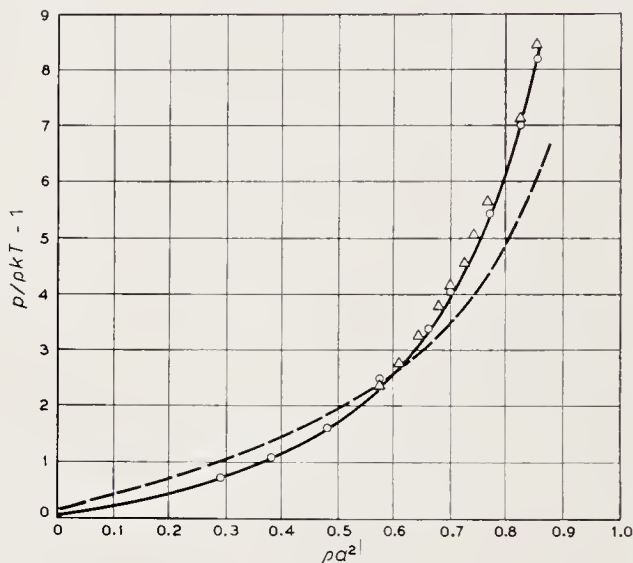


Fig. 12. Comparison of the theoretical equation of state with machine computations^{62,63} for a two-dimensional hard sphere fluid.

The approximate theory outlined in this section while giving excellent numerical agreement and considerable physical insight into the hard sphere fluid does not suggest an obvious answer to why the approximation made is so successful. For example, the limiting surface tension, $\sigma_0(\rho)$, given by Eq. (69) agrees exactly with the known first term of the density expansion of $\sigma_0(\rho)$,⁶⁰

$$\sigma_0(\rho) = -\frac{kT\pi a^4 \rho^2}{8} [1 + O(\rho)] \quad (75)$$

As yet no proof is available that $G(r, \rho)$ is non-decreasing for $r > a/2$ for all fluid densities. Without going into details, it should be mentioned that G does determine the behavior of $g(r)$ for some distance beyond $r = a$.^{3,41}

Helfand and Stillinger⁶⁴ have recently employed this theory to obtain a suitable "local density" correction of the superposition theory for the hard sphere system. While the numerical solution of the modified integral equation is not available at this time, the equation is unique among other approximate theories in yielding the exact value of the fourth virial coefficient.

For fluids possessing a finite-range attractive potential as well as a hard sphere cutoff, an entity analogous to the G function can be defined⁴ which determines the chemical potential of a fluid molecule and again is a solution of the direct analogs of the exact integral equations (59) and (61).

We have already in this and the previous sections made a number of comparisons between the various theories of fluids and the machine computations for the hard sphere system. Unfortunately, many recent developments in theory have been evaluated numerically only to the extent that the fourth and fifth virial coefficients can be compared. The table below lists the values of the fourth and fifth virial coefficients for the three-dimensional hard sphere fluid in units of the second virial coefficient b [cf. Eq. (33)]. The bases of calculation have been identified already in Section III except for the older "netted-chain" approximation of Rushbrooke and Scoins.⁶⁵

TABLE I. Estimates of the Fourth and Fifth Virial Coefficients for the Hard Sphere Fluid

Basis of calculation	B_4/b^3	B_5/b^4
True value ^{47,11}	0.2869	0.115 ± 0.005 (Monte Carlo)
Non-linearized Born-Green theory ^{49,51,66}	0.3424	0.1335
Netted-chain approximation ⁶⁵	$0.2969 = 19/64$	0.5655
Hyper-netted chain approximation ^{32,35}	0.2092	0.0493
$E'_{(1)}$ -approximation ³⁵	$0.2969 = 19/64$	0.1370
Scaled particle theory ³	$0.2969 = 19/64$	0.1211
Scaled particle modification of superposition theory ⁶⁴	(exact) 0.2869	—

It is interesting to note that three of the approximate theories, including the scaled particle theory, yield the same numerical value for the fourth virial coefficient estimate. The significance

of this is not readily apparent.* Again we see that the scaled particle theory comes out quite satisfactorily in this numerical comparison.

VI. DISCUSSION AND APPLICATIONS

The preceding sections of this chapter clearly reveal that while we are far from being able to give rigorously exact answers for the hard sphere system to the basic questions asked in the introduction, considerable progress has been made, particularly as regards the second of these questions. Accepting the machine-calculated equation-of-state data, the scaled particle theory reproduces the high pressure or "fluid" branch results within a few per cent. At lower fluid densities the superposition theory⁶⁷ or the numerical solution of the Percus and Yevick²⁸ equation appear to be also adequate.⁶⁸ At sufficiently high densities, but below close packing, the free-volume theory appears to represent the low pressure or "solid" branch of the machine-calculated equation-of-state data.¹ The most important lacuna in our knowledge of the hard sphere system centers about the proof of the existence, the exact location for an infinite system and the nature of the apparent phase transition between the two branches of the phase diagram. Intuitively suggestive, if approximate, descriptions of this transition, particularly if these can be related to the structure of the "fluid" and "solid" phases, would form a particularly valuable contribution.

An outstanding problem concerns itself with the "structure" of a hard sphere phase. This is a special instance of the more general difficulty of the specification of the structure of infinitely extended random media. These questions will perhaps be the subject of a future mathematical discipline—stochastic geometry. The pair correlation function $g(r)$, even if it is known, hardly suffices to specify uniquely the stochastic metric properties of a random structure. For a finite (N and V finite) system in equilibrium in thermal contact with a heat reservoir at temperature T , the density in the configuration space of the N particles [Eq. (2)]

* The reader interested in the diagrammatic basis of many of the approximations listed in Table I should consult Reference 35. See also the note added in proof at the end of the chapter.

gives as complete a specification of the structure as is consistent with the natural fluctuations inherently associated with the canonical distribution. Even for a finite system for which this density is known, with increasing N , mathematical difficulties rapidly prevent the explicit evaluation of any averages of functions of the locations of the particles. These difficulties are aggravated by existence problems in the limit as N and V become infinite while maintaining a constant total number density. The specification of short-range or long-range order parameters can be made relevant to a given measured physical property of a random medium yet no general (invariant) geometrical significance can usually be ascribed to such numbers). The nature of the density correlation among subsets of particles of a fluid is a very formal manner of description as compared with the structural concepts with which the classical crystallographer is used to dealing with solids.

Bernal⁶⁹ has recently presented some qualitative considerations concerning the geometrical disorder of fluids based on a hard sphere model. In accounting for the relatively small volume changes in going from typical solids to liquids, Bernal postulates that a simple (atomic) fluid (and in particular the hard sphere fluid at higher densities) may be viewed geometrically as an assembly of atoms in which all the near neighbors are approximately the same distance apart to within about 10%. From studies of random models of such collections of hard spheres he finds that the number of atoms surrounding a point chosen at random range from four to ten.⁶⁹ These lie at the corners of only five polyhedra, which are limited by having to have approximately equal lengths of their edges. The polyhedra (representing holes between atoms) can be fitted together in a large, but finite, variety of ways. Among these arrangements one must include pentagonal arrangements, e.g., pentagonal bipyramids, which must prevent the appearance of crystallographic long-range order. A liquid, in distinction to a solid, represents not a single structure but a series of possible structures of this kind whose stability is temperature-dependent.⁶⁹ This structural guess, while suggestive, is still far from being either verified or translated in any obvious way into a statistical quantitative theory of the macroscopic properties of fluids.

Granting the existence of the three-dimensional hard sphere "solid" phase in the infinite system, there still remains the problem of the kind of packing of the highly localized centers of the spheres. It seems unlikely that this question could be satisfactorily resolved by machine computations in view of their sensitivity to the number of spheres used and the initial geometry of their packing.¹ There are many distinct ways of close packing spheres of equal diameter. In two dimensions the densest close packing* of hard discs is known⁷⁰ to be the hexagonal close packing achieved by choosing the discs to be the incircles of the faces of the regular {6,3} tessellation. This corresponds to a density of $\pi/2\sqrt{3} = 0.9069 \dots$ In three dimensions the densest *regular* packing of spheres of equal diameter corresponds to the face-centered cubic or close-packed hexagonal lattice, both with density $\pi/3\sqrt{2} = 0.74048 \dots$ It is natural to ask whether some less systematic packing might have a greater density. This is still an open question. It is known⁷¹ that if such a packing exists, its density must be less than $0.7797 \dots$ If this is the case, then the possibility of another phase transition in the hard sphere system which has not been observed in the machine calculations cannot be excluded.† On the other hand, simple model experiments⁷² with randomly piled ball bearings have so far always yielded densities of close packing considerably less than 0.7405 . Thus it appears unlikely that any greater density can be maintained throughout a region that extends indefinitely in all directions. Even less is known about the geometry of random collections of hard spheres of unequal diameters, which would be of interest in connection with theories of certain mixtures and alloys.

The problem of finding effectively the equation of state of a mixture of hard spheres of different diameters, incidentally, is of considerable interest in a number of applications, e.g., for finding the high temperature equation of state of mixtures of real gases and the surface tension of mixtures, among other things. While a number of the theories of fluids mentioned in Section IV of this chapter can also be reformulated^{11,35,49} formally for mixtures,

* This is true even abandoning both the requirements that the packing be regular and that the centers of the discs form a lattice.

† Assuming the "solid" phase corresponding to the low pressure branch of the isotherm is a regular crystalline arrangement.

relatively few numerical evaluations have been made.^{73,74} The hard sphere potentials for the hard sphere components α, β are

$$\varphi_{\mu\nu}(r) = \begin{cases} \infty & r < r_{\mu\nu} \\ 0 & r \geq r_{\mu\nu} \end{cases} \quad (76)$$

with

$$r_{\mu\nu} = \frac{1}{2}(r_{\mu\mu} + r_{\nu\nu}) \quad \mu, \nu = \alpha, \beta$$

The equation of state can be easily expressed in a form analogous to Eq. (26), using the pair correlation functions $g_{\mu\nu}(r)$,⁴⁹

$$\frac{p}{\rho kT} = 1 - \frac{2\pi}{3} \rho \{ x_\alpha^2 r_\alpha^3 g_{\alpha\alpha}(r_{\alpha\alpha}) + 2x_\alpha x_\beta r_{\alpha\beta}^3 g_{\alpha\beta}(r_{\alpha\beta}) + x_\beta^2 r_\beta^3 g_{\beta\beta}(r_{\beta\beta}) \} \quad (77)$$

N_μ being the number of component μ hard spheres in the volume V , where $x_\mu = N_\mu/N$, $\mu = \alpha, \beta$. The second and third virial coefficients of this mixture have been evaluated exactly by McLellan and Alder.⁷⁴ In their notation,⁷⁴ one can again write, $\rho_\mu = N_\mu/V$,

$$g_{\mu\nu}(r_{\mu\nu}) = 1 + \rho_\alpha a_{\mu\nu} + \rho_\beta b_{\mu\nu} + \frac{1}{2}(\rho_\alpha^2 c_{\mu\nu} + 2\rho_\alpha \rho_\beta d_{\mu\nu} + \rho_\beta^2 e_{\mu\nu}) + \dots \quad (78)$$

Setting,

$$R = \frac{1}{2}(r_{\alpha\alpha} + r_{\beta\beta}), \quad r_{\alpha\alpha} = R(1 - \gamma), \quad r_{\beta\beta} = R(1 + \gamma) \\ v_0 = 2\pi R^3/3$$

and

$$a_{\alpha\alpha} = a_\alpha v_0, \quad a_{\alpha\beta} = a v_0, \quad a_{\beta\beta} = a_\beta v_0 \\ b_{\alpha\alpha} = b_\alpha v_0, \quad b_{\alpha\beta} = b v_0, \quad b_{\beta\beta} = b_\beta v_0$$

they find that

$$a_\alpha = \frac{5}{8}(1 - \gamma)^3, \quad b_\alpha = \frac{1}{8}(1 + \gamma)^2(5 - \gamma) \\ a = \frac{1}{8}(1 - \gamma)^3(5 + 3\gamma), \quad b = \frac{1}{8}(1 + \gamma)^3(5 - 3\gamma) \quad (79) \\ a_\beta = \frac{1}{8}(1 - \gamma)^2(5 + \gamma), \quad b_\beta = \frac{5}{8}(1 + \gamma)^3$$

These results were obtained by integrating the Born and Green integral equations using the superposition approximation. This procedure is, as in the pure fluid, exact only up to the third virial coefficient. The fourth virial coefficient is already inexact; actually the superposition approximation leads in this case to two

alternative expressions for the fourth virial coefficient which were numerically estimated,⁷⁴ and which become more divergent as the ratio of the diameters of the two spheres becomes larger. The free-volume theory leads to an error in the third virial coefficient for mixtures, as in the case of pure fluids. McLellan and Alder⁷⁴ have also tabulated to the indicated accuracy the important thermodynamic functions and the changes in these functions upon mixing at constant free volume.

Conformal (second-order) solution theory has been applied to a mixture of almost equal-sized hard spheres of diameters 1 and $1 + \rho$, $\rho \ll 1$, by Buchowski and Bellemans.^{74a} Denoting by n and x the number density and mole fraction of hard spheres of diameter 1 at temperature T and pressure p they find the exact low density result to terms of order ρ^2 for the molecular excess free energy g^E of the mixture

$$\frac{g^E}{x(1-x)kT\rho^2} = -\frac{3}{2} \left(\frac{2\pi}{3}\right) n + \frac{33}{32} \left(\frac{2\pi}{3}\right)^2 n^2 - 0.555 \left(\frac{2\pi}{3}\right)^3 n^3 + O(n^4) \quad (79a)$$

Thus g^E is *negative* at low densities as is the molecular excess volume $v^E = dg^E/dp$. A high density estimate of g^E is obtained^{74a} by (1) assuming that the triplet correlation function of any particles 1, 2, 3 is such that particles 2 and 3 are uncorrelated except for the fact that they may not overlap, and (2) the use of Eqs. (68) and (45) for the pair correlation function on contact of the hard spheres of diameter 1. This approximate computation indicates that the sign of g^E (and v^E) undergoes an inversion as the density increases. This implies that a mixture of hard spheres will separate into two phases at sufficiently high p and low T , e.g., the predicted miscibility gap for $\rho = 0.1$ occurs for $n \simeq 1.1$.^{74a}

A critical review of these results as well as several other novel approaches to theories of mixtures evaluated for mixtures of hard spheres has been presented by Salsburg and Fickett.^{74b} These authors also compare the various theories numerically particularly for the diameter ratio $5/3$ used by Smith^{74c} for his preliminary (low density) Monte Carlo calculations of binary hard sphere mixtures. Salsburg and Fickett^{74b} conclude for these systems that

ideal mixing is probably a very good approximation at low to medium densities, but at higher densities (where the miscibility gap, if any, is expected) the problems remain essentially unsolved.

The behavior of one-dimensional mixtures of hard spheres of different diameters a_1 and a_2 follows directly from the exact validity of the quasi-chemical approximation for the one-dimensional combinatorial factor for particles interacting only with their nearest neighbors.* Unfortunately, this result is valid only for one-dimensional systems. It would be of considerable interest to extend the scaled particle theory to deal with mixtures of hard spheres.

The availability of the machine-computed results for thermodynamic functions, particularly for the pressure of collections of a small number, N , of particles in a periodic box, has recently added impetus to the study of the thermodynamic properties of small systems. The exact N -dependence of the first two virial coefficients, for example, has been given explicitly by Oppenheim and Mazur.⁷⁶ Lebowitz and Percus⁷⁷ investigated more generally the dependence of the pressure of a homogeneous system subject to periodic boundary conditions, at a given density and temperature, on N . The particles of these systems are to interact via forces of finite range a , a particular case in point being the hard sphere system. There are two types of N -dependences of intensive properties: (1) a simple dependence in the form of a power series in $(1/N)$ which can be explicitly computed in terms of grand-ensemble averages of these properties where it is absent, and (2) a complex dependence arising from the volume dependence of those cluster integrals which are large enough to wind at least once around the periodic torus. The latter affect the virial series terms $k > (N/\rho a^3)^{1/2}$ and play, for example, a dominant role in the N -dependence observed by Alder and Wainwright in their machine computations on the hard sphere fluid. As yet no explicit calculation of the latter N -dependences exists.

* The equation of state of this one-dimensional mixture can also be easily derived by considerations similar to those which led to Eq. (47) to give the "free volume" expression

$$p/kT = \rho/[1 - \rho(x_1 a_1 + x_2 a_2)]$$

with $x_i = N_i/N$, $\rho = N/L$.

An open problem is the asymptotic behavior (with increasing n) of the virial coefficients B_n of the hard sphere fluid. Since the only forces in this system are repulsive, it was conjectured that all the virial coefficients are necessarily positive. While this classical conjecture has neither been disproven nor verified the basis for it is untenable. Thus, the sixth virial coefficient of a fluid composed of three-dimensional hard cubes in which the forces are all repulsive is negative.⁷⁸

This necessarily sketchy outline of the unsolved problems relating to this system is certainly not complete. We have mainly endeavored to give the reader a sampling of the variety of the open theoretical questions. We conclude this chapter with a small selection of the varied applications of this mathematically idealized theory for the description of thermodynamic properties of real fluids.

We have already mentioned in the Introduction that the behavior of real fluids can be expected to be dominated by the behavior of the hard cores of the fluid molecules either (a) at sufficiently high temperatures or (b) at sufficiently high fluid densities, for the physically plausible reasons already stated. We shall now see that mathematically the hard core dominance of, say, the high temperature equation of state of the fluid is justifiable from a simple high temperature expansion, commonly used in somewhat different statistical mechanical contexts, of the configurational partition function. This expansion results when the "soft" part of the intermolecular potential $\varphi_s(r)$ is treated as a perturbation of the hard core (hard sphere) potential, $\varphi_h(r)$. Zwanzig⁷⁹ has studied these expansions in some detail, but we shall need only the first term, which has been investigated numerically and compared with experiment by Alder and Smith.⁸⁰ Equilibrium properties of dense fluids, e.g., compressibility, surface tension, heat of vaporization, etc., on the other hand, explicitly involve an estimate of the reversible work required to form a spherical cavity sufficiently large to accommodate the hard core of another fluid molecule, or more generally that of a hard sphere solute. The mathematical functional form of this reversible work is certainly closely approximated for sufficiently large cavities by the sum of a pressure-volume contribution and a surface tension-surface area contribution as in the hard sphere scaled

particle theory;⁴⁰ while for cavities sufficiently small to contain only one fluid core this reversible work done on the real fluid is precisely given by this entity computed only for the hard cores of the real fluid molecules. Reiss, Frisch, Helfand and Lebowitz⁴⁰ have compared with experiment a number of estimated equilibrium properties of typical liquids based on this ansatz and Stillinger has employed the same theory in accounting for the compressibility⁸¹ and surface tension of simple molten salts.⁸²

Turning first to the high temperature expansion, one writes^{79,80} the intermolecular potential between two real fluid molecules $\varphi(r)$ as a sum of a hard core (rigid sphere) potential $\varphi_h(r)$ given by Eq. (24) and a remaining "soft" part $\varphi_s(r)$ which vanishes for $r < a$, where a is the diameter of the hard core. Alder and Smith⁸⁰ chose for $\varphi_s(r)$ a truncated Lennard-Jones⁶⁻¹² potential with ε the characteristic energy and σ the characteristic distance parameter. The location of the hard sphere cutoff is determined by the ratio $c = a/\sigma$, which was treated as an adjustable parameter (varying slightly with temperature) in fitting the data. Thus

$$\varphi_s(r) = \begin{cases} 0 & \text{for } r < a = \sigma c \\ 4\varepsilon \left(\frac{\sigma^{12}}{r^{12}} - \frac{\sigma^6}{r^6} \right) & \text{for } r > a = \sigma c \end{cases} \quad (80)$$

and

$$\varphi(r) = \varphi_h(r) + \varphi_s(r) \quad (81)$$

The total potential energy of the N molecules of the fluid contained in the volume V can then be written

$$\begin{aligned} U &= \frac{1}{2} \sum_{i \neq j}^N \varphi_h(r_{ij}) + \frac{1}{2} \sum_{i \neq j}^N \varphi_s(r_{ij}) \\ &= U_h + U_s \end{aligned} \quad (82)$$

When this potential is substituted in the configuration partition function (3) and the result divided by $N!$ we obtain the negative

exponential of the configurational Helmholtz free energy A divided by kT , viz.,

$$\begin{aligned}\exp(-\beta\bar{A}) &= (N!)^{-1} \int \dots \int_V^{(N)} \exp(-\beta U) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &= (N!)^{-1} \int \dots \int_V^{(N)} \exp(-\beta U_k) \exp(-\beta U_s) d\mathbf{r}_1 \dots d\mathbf{r}_N\end{aligned}\quad (83)$$

Expanding $\exp(-\beta U_s)$ formally in a power series in $+\beta U_s$ and retaining only the first two terms, i.e., treating βU_s as a small perturbation, one finds

$$\begin{aligned}\exp(-\beta\bar{A}) &= (N!)^{-1} \int \dots \int_V^{(N)} \exp(-\beta U_h) [1 - \beta U_s + \dots] \\ &\quad d\mathbf{r}_1 \dots d\mathbf{r}_N = (N!)^{-1} \int \dots \int_V^{(N)} \exp(-\beta U_h) d\mathbf{r}_1 \dots d\mathbf{r}_N \\ &\quad \times \left[1 - \frac{\beta}{2} \sum_{i \neq j}^N \frac{\int \dots \int_V^{(N)} \exp(-\beta U_h) \varphi_s(r_{ij}) d\mathbf{r}_1 \dots d\mathbf{r}_N}{\int \dots \int_V^{(N)} \exp(-\beta U_h) d\mathbf{r}_1 \dots d\mathbf{r}_N} + \dots \right] \\ &= \exp(-\beta\bar{A}_h) \\ &\quad \times \left[1 - \frac{\beta}{2} \sum_{i \neq j}^N \frac{\int \dots \int_V^{(N)} \exp(-\beta U_h) \varphi_s(r_{ij}) d\mathbf{r}_1 \dots d\mathbf{r}_N}{\int \dots \int_V^{(N)} \exp(-\beta U_h) d\mathbf{r}_1 \dots d\mathbf{r}_N} + \dots \right]\end{aligned}\quad (84)$$

where

$$\exp(-\beta\bar{A}_h) = (N!)^{-1} \int \dots \int_V^{(N)} \exp(-\beta U_h) d\mathbf{r}_1 \dots d\mathbf{r}_N \quad (85)$$

and $\bar{A}_h$ is the configurational free energy of the hard sphere fluid composed of the hard cores of the fluid molecules. Since the hard cores are physically indistinguishable, we can carry out the summation in Eq. (84) and using Eq. (5) express Eq. (83) in terms of the hard sphere pair correlation function $g_h(r)$,

$$g_h(r_{12}) = \frac{V^2 \int \dots \int \exp(-\beta U_h) d\mathbf{r}_3 \beta \dots d\mathbf{r}_N}{\int \dots \int \exp(-\beta U_h) d\mathbf{r}_1 \dots d\mathbf{r}_N} \quad (86)$$

as follows

$$\exp(-\beta \bar{A}) = \exp(-\beta \bar{A}_h) \left[1 - \frac{\beta N(N-1)}{2V^2} \int g_h(r_{12}) \varphi_s(r_{12}) d\mathbf{r}_1 d\mathbf{r}_2 + \dots \right] \quad (87)$$

For sufficiently large temperatures, to first order in β , the logarithm of the square bracket in Eq. (87) can be expanded and we find^{79,80} ($N-1 \simeq N$)

$$\bar{A} = \bar{A}_h + \frac{2\pi N^2}{V} \int_0^\infty g_h(r) \varphi_s(r) r^2 dr + O(\beta) \quad (88)$$

Differentiating this equation with respect to V , we have using one of the Maxwell thermodynamic identities

$$p = p_h - \frac{\partial}{\partial V} \left[\frac{2\pi N^2}{V} \int_0^\infty g_h(r) \varphi_s(r) r^2 dr \right] \quad (89)$$

with p_h the pressure of the equivalent hard sphere gas of molecular cores. Thus, to the first order in $1/kT$, a knowledge of the hard sphere pair correlation function [and thus of p_h as well via Eq. (26)] allows one to find the high temperature equation of state of any fluid up to a quadrature.

For low or moderately high fluid densities one can take⁸⁰ for $g_h(r)$ the virial equation (34). Using this and Eq. (80) for φ_s , Alder and Smith⁸⁰ find the high temperature equation of state from (89) to be

$$\frac{pV}{NkT} = b + \frac{a^*}{T^*} \quad (90)$$

where T^* is the reduced temperature $T^* = kT/\varepsilon$. The intercept,

$$b = \left(\frac{pV}{NkT} \right)_h = 1 + \frac{2.0944c^3}{v^*} + \frac{2.7416c^6}{v^{*2}} + \frac{2.6358c^9}{v^{*3}} + \frac{2.2122c^{12}}{v^{*4}} \quad (91)$$

is the hard sphere entity which is taken in sufficient approximation to be given by the five-virial-coefficient hard sphere equation of state (32), with v^* the reduced volume, $v^* = V/N\sigma^3$. The slope a^* is given by the virial formula

$$a^* = \frac{1}{c^6} \left[-\frac{5.5850c^3}{v^*} - \frac{5.4701c^6}{v^{*2}} + \frac{0.8262c^9}{v^{*3}} \right] + \left(\frac{1}{c^{12}} - \frac{1}{c^6} \right) \left[\frac{2.7925c^3}{v^*} + \frac{5.8448c^6}{v^{*2}} + \frac{5.8526c^9}{v^{*3}} \right] \quad (92)$$

The isotherms of this perturbation high-temperature equation of state lead surprisingly to a critical point and a van der Waals loop in a gas-liquid phase equilibrium. While this occurs well beyond the range of validity of the derivation, the critical point data are astonishingly good⁸⁰

$$p_c^* = 0.19, \quad T_c^* = 1.4, \quad v_c^* = 3.3, \quad \left(\frac{p^* v^*}{T^*} \right)_c = 0.44$$

as compared, say, with the experimental results for argon which are

$$p_c^* = 0.12, \quad T_c^* = 1.3, \quad v_c^* = 3.2, \quad \left(\frac{p^* v^*}{T^*} \right)_c = 0.29$$

The applicability of the equation of state (90) to experimental data is shown in Fig. 13 for 1 mole of argon, at various volumes.

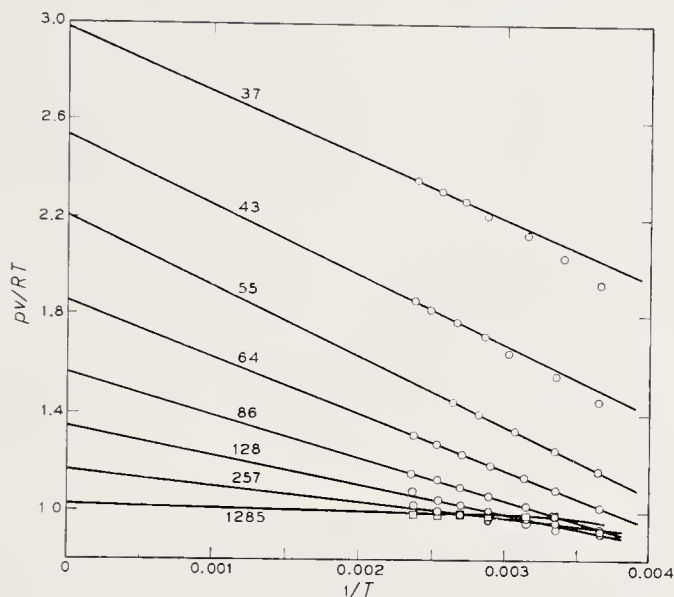


Fig. 13. The experimental high temperature equation of state for argon; the figures associated with the lines refer to the various volumes of the fluid in cc.

Intercepts b and slopes a^* are obtained from these straight lines. Figures 14 and 15 present in turn a comparison of the experimental intercepts and slopes with the theoretical virial lines given by Eq. (91) and Eq. (92) for a variety of gases. With the proper choice of c in Eq. (80) the agreement is very good. The physical reason for the apparent cancellation of higher perturbation contributions to the equation of state, which one would otherwise expect are needed in this density and temperature range, follows from the typical insensitivity of the dense gas or liquid pair correlation function to temperature at constant volume. For real molecules, $g(r)$ changes with temperature at low density (and at constant volume) because clustering is possible at sufficiently low temperatures. At higher densities the molecules are almost touching and little further clustering is possible. Some slight change in $g(r)$ is also possible with increasing temperature (and thus increasing mean

kinetic energy per molecule) due to further penetration into the repulsive potential. The proper choice of the hard sphere cutoff c can take account of this effect.⁸⁰

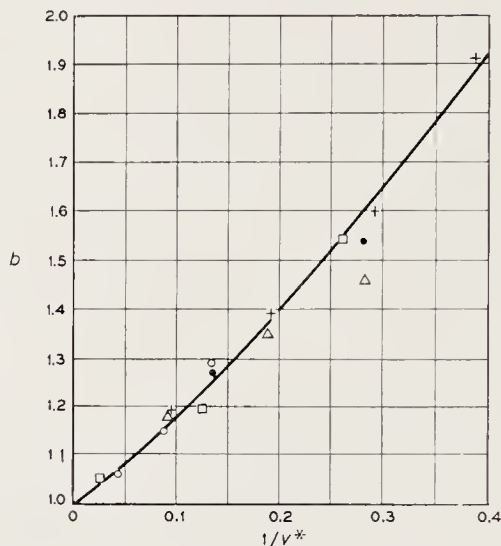


Fig. 14. Comparison of the experimental constant term $(pV/RT)_h = b$ with the theoretical virial line for $c = 1/1.10$ for a variety of gases.

□ water; △ methane; ○ helium; + xenon; ● carbon dioxide.

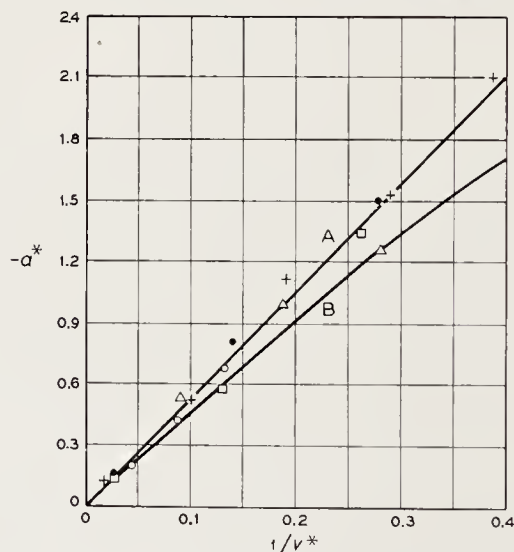


Fig. 15. Comparison of the theoretical and experimental first-order perturbation terms, $-a^*$, for various gases, using the virial theory for $c = 1/1.10$ (solid line B) and $c = 1/1.08$ (solid line A). □ water;

△ methane; ○ helium; + xenon; ● carbon dioxide.

We now turn to the computation of various thermodynamic properties of *dense* fluids and their solutions composed again of spherical molecules possessing a rigid core of diameter a . It suffices to consider the chemical potential, μ , of an added spherical solute molecule whose hard core diameter is b and whose intermolecular potential φ is the sum of a hard sphere potential φ_h and a "soft" part φ_s . φ_h is infinite for intermolecular distances less than $\frac{1}{2}(a + b)$ and vanishes for larger distances. An important special case arises when $b = a$ for then we are adding just another "solvent" molecule as when we are dealing with a pure fluid. We can now add the solute molecule to the "solution" in two stages. In the first stage we form a mobile spherical cavity, devoid of molecular "solvent" fluid centers of radius $r = \frac{1}{2}(a + b)$, which is just large enough to accommodate the hard core of the "solute" molecule. The reversible work which has to be expended to do this is $\mu_h[\frac{1}{2}(a + b)]$ where⁴⁰

$$\mu_h[\frac{1}{2}(a + b)] = kT \ln \rho_2 \Lambda_2^3 + W[\frac{1}{2}(a + b)] \quad (93)$$

with W the reversible work required to form a (rigid) spherical cavity of the indicated radius, and ρ_2 and Λ_2 the density and mean thermal de Broglie wavelength of the "solute."

Following Reiss, Frisch, Helfand and Lebowitz,⁴⁰ the calculation of the work W follows almost directly from their previous considerations outlined in Section V. For a sufficiently large radius r the work of cavity formation in any fluid is the sum of the volume expansion and surface tension work

$$\frac{dW(r)}{dr} \sim 8\pi\sigma r + 4\pi p r^2 \quad (94)$$

with p the actual pressure, σ the dense fluid. On the other hand, for cavities with r smaller than $a/2$, the scaled particle theory [cf. Eq. (53) together with Eq. (42)] give the work exactly as^{3,23}

$$W(r) = -kT \ln (1 - 4\pi r^3 \rho / 3) \quad 0 \leq r \leq a/2 \quad (95)$$

since at most one fluid molecule center may occupy such a cavity. For $r > a/2$, but still considering microscopic cavities whose radii of curvature are comparable with the range of molecular sizes,

the curvature dependence of the surface tension must be taken into account. Thus Eq. (94) is replaced by the cubic polynomial in r suggested by the scaled particle theory,

$$W(r) = \left(\frac{4\pi}{3} r^3\right) p + 4\pi r^2 \sigma_0 \left[1 - \left(\frac{2\delta}{r}\right)\right] + K_0 \quad (96)$$

where the functions σ_0 , δ and K_0 of ρ , T and p must still be determined. This is easily done using Eq. (95) and the fact that W and its first r derivative must be continuous at $r = a/2$. Again, setting $y = \pi a^3 \rho / 6$, we find the limiting surface tension against a rigid planar interface σ_0 to be⁴⁰

$$\sigma_0 = \left(\frac{kT}{4\pi a^2}\right) \left[\frac{12y}{1-y} + 18 \left(\frac{y}{1-y}\right)^2\right] - \frac{pa}{2} \quad (97)$$

as well as

$$\delta = \frac{a}{4} \left\{ \frac{[6y/(1-y)] + 18[y/(1-y)]^2 - (\pi p a^3 / kT)}{[6y/(1-y)] + 9[y/(1-y)]^2 - (\pi p a^3 / kT)} \right\} \quad (98)$$

and

$$K_0 = kT \left\{ -\ln(1-y) + \frac{9}{2} \left[\frac{y}{(1-y)} \right]^2 \right\} - \frac{\pi p a^3}{6}$$

In the second stage in the addition of the "solute" molecule to the "solution", the soft part of the intermolecular solute-solvent potential is charged using again a suitable coupling parameter ξ in terms of which we write

$$\varphi = \varphi_h + \xi \varphi_s(r) \quad (99)$$

This leads to the finally complete expression for the chemical potential of the "solute" molecule⁴⁰

$$\begin{aligned} \mu &= \mu_h + \int_0^1 d\xi \int_0^\infty 4\pi r^2 \varphi_s(r) g(r, \xi) dr \\ &= \mu_h + \mu_s \end{aligned} \quad (100)$$

where $g(r, \xi)$ is the radial distribution function of the "solute" in the fluid for the indicated value of the coupling parameter ξ . With φ_s the relatively weakly attractive part of the intermolecular

potential (i.e., φ_s is negative) for simple nonpolar fluids, $g(r, \xi)$ positive, μ_s is an essentially small, negative correction which must be added to the hard sphere contribution μ_h , dominant at high densities, arising from the rigid core. It is sometimes possible in calculating certain properties from Eq. (100) to eliminate μ_s in terms of an experimentally measured physical property. For example, if we wish to compute the heat of vaporization, λ_v , of a liquid whose vapor is ideal we may do so in terms of the experimentally determined coefficient of thermal expansion, α , at the boiling point. Using a somewhat lengthy but straightforward thermodynamic argument, which is fully given in Reference 40, one finds

$$\lambda_v \simeq kT + kT^2\alpha[(1 + 2y)^2/(1 - y)^3] \quad (101)$$

with neglect only of terms of the order of the very small pressure-volume work in the condensed liquid. This expression for λ_v is essentially an exact consequence of the assumed form of μ_h given by the scaled particle theory. It thus serves as an important criterion of the validity of our μ_h . Of course, reliable experimental values of α and a are needed in making comparisons with the theory and they are available for argon and methane. Table II summarizes the comparison between the experimental and calculated normal heats of vaporization for these two substances.

TABLE II. Comparison of Normal Heats of Vaporization⁴⁰

Substance	λ_v in calories, calcd. from (101)	λ_v in calories, exptl.
Ar	1510	1558
CH ₄	2280	2218

The agreement is very good.

Alternatively, one can neglect the contribution μ_s altogether and compare directly the extent to which the behavior of a given property of a sufficiently dense fluid is determined solely by its molecular rigid cores. Thus, given a gaseous solute which

approximates sufficiently closely a hard sphere solute, we can estimate $W(r)$ from a knowledge of Henry's law constant

$$k_H = p_2/\rho_2 \quad (102)$$

and compare it with the $W(r)$ given by Eqs. (96)–(98). For a nearly hard sphere solute, μ in solution, given essentially by the μ_h of Eq. (93), is also equal to the chemical potential of the solute in the vapor phase, μ_2 ,

$$\mu_h \approx \mu = \mu_2 = kT \ln (p_2 \Lambda_2^3/kT) \quad (103)$$

The last equality is a consequence of the assumed ideality of the vapor. Comparing Eqs. (93), (102) and (103) we thus find

$$W(r) \approx kT \ln (k_H/kT) \quad (104)$$

Table III presents a comparison of $W(r)$ calculated from Eq. (104) and $W(r)$ given by Eq. (96) for helium in two solvents.*

TABLE III. Reversible Work of Cavity Formation and Henry's Law Constant⁴⁰

System	T	$W(r)$ from Eq. (96)	$kT \ln (k_H/kT)$
He in Ar	86.6°K	6.07×10^{-14} erg	3.46×10^{-14} erg
He in benzene	288°K	1.73×10^{-13} erg	1.59×10^{-13} erg

In view of the sensitivity of the formulas to the exact value of a used and the uncertainty in ascribing the same a value obtained by measurement of one property to the determination of another, the agreement shown above is quite satisfactory.

Another check on the validity of our considerations is afforded by a comparison of σ_0 given by Eq. (97) with the surface tensions of typical non-polar liquids. These two entities are not the same since the actual liquid surface tension is the interfacial tension between a liquid and its vapor. At temperatures sufficiently far below the critical temperature of the liquid, where the vapor is

* In view of the neglect of the negative μ_s one expects

$$W(r) \geq kT \ln (k_H/kT).$$

highly attenuated, the two surface tensions should be at least of the same order of magnitude. As Table IV shows, the agreement here is considerably better than expected.

TABLE IV. Comparison of the Surface Tensions of Liquids Below Their Normal Boiling Points⁴⁰

Substance	Temp., °K	σ_{exp} (dynes/cm)	σ_0 (dynes/cm)
Ne	27.2	4.80	6.09
Ar	85.1	13.2	16.4
He	4.2	0.098	0.223
H ₂	20.4	1.80	1.91
N ₂	70.1	10.5	14.9
O ₂	70.1	18.3	23.6
C ₆ H ₆	273.1	29.02	34.3

It is of some interest that even the presence of long-range forces, such as the Coulombic ones present in simple fused salts, does not force us to contradict the conjecture that the pair correlation function of a dense fluid is virtually equal to that of a fluid composed of the uncharged cores. Stillinger⁸¹ has aptly summarized the arguments in support of this contention for fused salts and we cannot afford the space to repeat these arguments here. In particular, he has shown that the extension of Fowler's approximate evaluation of liquid surface tension to molten salts of the symmetrical valence type yields:⁸¹

$$\sigma \simeq -\frac{\pi k T c^2 a^4}{2} g_h(a) + \frac{c(z e)^2}{16D} \quad (105)$$

where c is the number concentration of either ionic species, z the number of charges carried by the ions, D the dielectric constant and $g_h(a)$ the scaled particle theory pair correlation function on contact of the rigid ion cores (i.e., a is the anion-cation distance of nearest approach),

$$g_h(a) = (4 - 2y + y^2)/4(1 - y)^3 \quad y = \frac{\pi}{3} c a^3 = \frac{\pi}{6} \rho a^3 \quad (106)$$

There is no unambiguous way of testing Eq. (105) because there is no unique way of choosing a dielectric constant. D may, however, be estimated from the square of the refractive index of the lower temperature solid phase when account is taken (by means of a Clausius–Mozotti relation) of the volume increase on melting. A typical computation may be carried out⁸³ for NaCl at 800°C and 1000°C. Choosing a to be 2.4×10^{-8} cm and $D = 2$ the results are:

	800°C	1000°C
σ (dynes/cm)	77	70
σ_{exp} (dynes/cm)	116.4	97.8

The agreement is only modest but the temperature dependence is correct. The sensitivity of Eq. (105) to the chosen values of a and D would allow improved agreement with small appropriate changes in these values.

Stillinger⁸² has further used the scaled particle hard sphere results to compute the isothermal compressibility,

$$\kappa = -\frac{1}{V} \left(\frac{\partial V}{\partial p} \right)_T \quad (107)$$

of such simple fused salts. Differentiating Eq. (68) he finds

$$\rho k T \kappa = (1 - y)^4 / (1 + 2y)^2 \quad (108)$$

Using the experimental values, at given T , of ρ and κ for the fused salts he finds a unique $y = \pi \rho a^3 / 6$ for each molten salt and thus a value of a , the anion–cation collision diameter, which can then be compared with a computed as the corresponding sum of crystal radii. The results of this comparison are summarized in Table V.

TABLE V.⁸² Values of the Anion-Cation Collision Diameter Computed from the Fused Salt Isothermal Compressibilities. The Corresponding Sums of Pauling Ionic Crystal Radii Appear in Parentheses. All Distances are in Ångstrom Units

$T^{\circ}\text{C}$	600	700	800	900	1000	Gas distance
LiCl (2.41)		2.31	2.26	2.20	2.14	2.013
NaCl (2.76)			2.47	2.41	2.34	2.361
KCl (3.14)			2.70	2.63	2.55	2.666
CsCl (3.50)		3.01	2.93	2.84	2.74	2.906
LiBr (2.55)	2.55	2.49	2.43	2.38	2.31	2.167
NaBr (2.90)			2.63	2.58	2.51	2.514
KBr (3.28)			2.85	2.78	2.70	2.82
CsBr (3.64)		3.06	2.98	2.88	2.75	3.06
NaI (3.11)		2.88	2.82	2.74	2.66	2.742
KI (3.49)		3.09	3.01	2.93	2.82	3.048
CdCl ₂ (2.78)	2.50	2.45	2.39			

Stillinger⁸² notes the fact that the computed distances a for each homologous series retain the correct increasing order as one travels down the periodic table. This increase parallels the increase of the ionic atomic number in the given series. The smaller ions, as expected from their electronic structure, behave more nearly as rigid spherical particles, as can be seen from their considerably smaller temperature variation of a .

Reiss and Mayer⁸⁴ and Mayer^{85,86} have also made extensive computations of values of the surface tension of molten ionic salts,⁸⁴ liquid metals,⁸⁵ and simple nonpolar and polar liquids⁸⁶ using Eq. (97) or simple modifications thereof, obtaining results in remarkable agreement with experimental values.

Note Added in Proof

Since this chapter was submitted in January, 1962, a number of investigations dealing with the hard sphere fluid have appeared, in particular, those based on the Percus-Yevick (P.Y.) integral equation.²⁸ This equation is the simplest and, on the basis of

numerical comparisons made so far, is at least as satisfactory as the other approximate integral equations reviewed in Section III. For three-dimensional hard spheres, this equation is

$$\tau(\mathbf{r}) = 1 + \rho \int \tau(\mathbf{r}') d\mathbf{r}' - \rho \int \tau(\mathbf{r}') \tau(\mathbf{r} - \mathbf{r}') d\mathbf{r}'$$

$$\begin{array}{ll} |\mathbf{r}'| < a & |\mathbf{r}'| < a, \\ & |\mathbf{r} - \mathbf{r}'| > a \end{array} \quad (109)$$

where $\tau(\mathbf{r})$, the P.Y. function, is related to the direct correlation function $C(\mathbf{r})$ of Ornstein and Zernike and the pair distribution function $g(\mathbf{r})$ by

$$\begin{array}{ll} g(\mathbf{r}) = 0 & (0 < r < a) \\ g(\mathbf{r}) = \tau(\mathbf{r}) & (a < r < \infty) \\ C(\mathbf{r}) = -\tau(\mathbf{r}) & (0 < r < a) \\ C(\mathbf{r}) = 0 & (a < r < \infty) \end{array} \quad (110)$$

This P.Y. equation (109) has been solved by Wertheim,⁸⁷ and the resulting equation of state, obtained in closed form, was found to be identical with the "scaled particle" theory result,³ Eq. (68). The P.Y. hard sphere direct correlation

$$C(\xi) = -(1 - y)^{-4}[(1 + 2y)^2 - 6y(1 + \frac{1}{2}y)^2\xi + y(1 + 2y)^2\xi^3/2], \quad \xi < 1 \quad (111)$$

The reader is referred to the article by Wertheim⁸⁷ for the detailed form of the P.Y. $g(r)$.

Earlier, Stell⁸⁸ had shown that the P.Y. equation gives the exact one-dimensional hard "sphere" (rod) equation of state.⁴⁴ Furthermore, Stell⁸⁸ has shown that the P.Y. equation can be associated with an exact equation for $g(r)$ containing an infinite series that provides a systematic means, in principle, of improving the P.Y. equation through iterative partial summations of the graphs associated with $g(r)$. Thus, a diagrammatic basis for the P.Y. equation is obtained which is similar but not identical to the hyper-netted chain approximation equations.³⁰⁻³⁷ The comparison of the retained diagrams, together with the Wertheim⁸⁷ solution of the P.Y. equation, provides a complete diagrammatic explanation of the numerical coincidences of Table I, first noted in this chapter.

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STUDIES IN THE KINEMATICS OF ISOTHERMAL DIFFUSION. A MACRO-DYNAMICAL THEORY OF MULTICOMPONENT FLUID DIFFUSION

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I. THE PROBLEM AND THE METHOD

In chemical kinetics the concept of the order of a reaction forms the basis of a kinematics which constitutes a frame for most of the molecular theories of chemical reactions. The fundamental magnitudes of this kinematics are the concentrations and the specific rate constants. In simple cases only the time enters as an independent variable, whereas in a diffusion process both time and space are involved. Diffusion processes are generally described in terms of diffusion coefficients, volume concentrations and thermodynamic potential or activity factors. Partial volume factors and friction coefficients associated with the components of the diffusing mixture are also essential in the description. A feature of the macro-dynamical theory is that it covers any region of concentration. Especially simple equations are connected with the *differential* diffusion process (diffusion with small concentration differences), for which the different coefficients or factors mentioned above are practically constant.

The differential diffusion coefficients are characteristic of any mechanically normal and chemically stable equilibrium mixture; they represent properties of state. This reminds us of the necessity in (non-dilute) chemical kinetics of assuming a small change, so that the "medium effects" will not turn the rate constants into variables of time. This fact regarding the elementary description of a chemical reaction rate is not always explicitly stated in the texts. The reasons may be that a chemical change has often been conveniently measured only in a rather limited concentration range of the reactants and that most experiments have been confined to dilute solutions. If this simplification were not introduced, the kinematics in question would, for instance, contain partial volumes.

The theory presented here resolves itself into a generalization of the well-known Nernst-Einstein equation ($D = RT/\Phi$) to several components and optional concentration characteristics. The cases of two- and three-component mixtures are treated in detail. The latter case is also shown to be of interest in treating self diffusion in a binary mixture, a system which results from letting two components become diffusionally identical although still distinguishable.

On the whole, the solutions to our Eqs. (1)–(7) are exact in a sense which would not be maintained in an extension to large concentration differences in a volumetrically non-ideal system.

Multicomponent diffusion has also been treated in ways other than the one described here, namely by the methods of irreversible thermodynamics and statistical mechanics. However, the results throughout seem to be completely consistent, as shown by Ljunggren.²² It is true that Coleman and Truesdell² have expressed the opinion that the phenomenological procedure of irreversible thermodynamics still lacks full conclusiveness when applied to continuous processes, but no cases of misleading conclusions are known, probably because they are immediately abandoned as obviously wrong. In any case, for our special type of problem the macro-dynamical treatment described below is far-reaching and of general applicability (e.g., also in the field of membrane diffusion,³² gel diffusion,³¹ and swelling). A limitation of the well-known Onsager²⁶ approach and similar procedures is the lack of explicit application of the very useful and physically

important concept of molecular or component friction. For example, the so-called phenomenological coefficients are naturally expressed and explained in terms of frictional coefficients. For analogous reasons, in other connections also, the usual phenomenological approach deals with only one side of the problem. However, in the case of diffusion, the step from one treatment to the other is really very short (see References 25, 26, 18, 22 and Prigogine²⁷).

Molecular frictions (or resistivities) also play a role in the statistical mechanics of the liquid state.¹ To what extent the step has been taken from molecular to *molar* properties of the components of a complex structure has in this case, as well as in the case of irreversible thermodynamics, been too little discussed. The problem is treated in Section VI of the present article.

II. GENERAL FORMULATION OF MULTICOMPONENT DIFFUSION

The equation^{9,18}

$$c_i \left(-\frac{\partial \mu_i}{\partial x} \right)_t - \sum_{j=1}^k (C_i - C_j) \phi_{ij} = 0 \quad (1)$$

is valid for a component i , where c is the concentration in mole/cm³, ϕ is the friction per cm³ of the mixture containing the components $i = 1 \dots k$, C is the component velocity J/c (where J is the flow), μ is the chemical potential or Gibbs' partial molar free energy, and $-(\partial \mu / \partial x)$ is the diffusion force in the diffusion direction x . This equation expresses the fact that the driving force acting on the component i in 1 cm³ of the mixture and the sum of the $k - 1$ friction forces on the component cancel.

In defining the velocity, e.g. of water in ethanol, as the flow divided by the concentration, we have assumed a slow process, so that the components are practically in internal equilibrium. This assumption is also necessary from other points of view, e.g. for the use of a conventional thermodynamic magnitude for the diffusion force.

As described in the introduction, the fundamental diffusion problem involves the use of partial volume factors⁴ which are

independent of time and space, i.e. a process without local bulk flow is assumed. The important condition²⁵

$$\sum C_i c_i \bar{v}_i = 0 \quad (2)$$

(where $\bar{v}$ is the partial molar volume) at the same time excludes a (trivial) total flow of the system. The equation is understood to define a common reference coordinate for the velocities, or for the flows Cc (compare Lamm¹⁷).

By a summation of all the expressions (1) an identity is obtained, because $\phi_{ij} = \phi_{ji}$ and $\sum_1^k c_i d\mu_i = 0$. Hence Eq. (1) represents $k - 1$ independent relations. Together with Eq. (2) we have k equations for defining the k velocities C_i .

The thermodynamic properties of Eq. (1) must be determined by the introduction of thermodynamic coefficients obtained from separate experiments. One possible and fundamental definition of such coefficients is

$$B_{ij}^X = \left(\frac{\partial \ln a_i}{\partial \ln X_i} \right)_{X_k} = 1 + \left(\frac{\partial \ln f_i}{\partial \ln X_i} \right)_{X_k} \quad (3)$$

where X_i is the mole fraction, a_i is the activity defined by $\mu_i = \mu_i^0 + RT \ln a_i$, μ_i^0 is the chemical potential in the standard state $a_i = 1$, k for all components except i and j , and f is the activity coefficient defined by $a_i = f_i X_i$. However, at least for the three-component case (see below), the use of *volume fractions* $Y = c\bar{v}$ instead of X in Eq. (3) is preferable.¹⁹

Like chemical potentials, neither velocities nor flows can be directly observed during ordinary diffusion experiments. (The nearest to being determined directly are the flows. The development of magnetic resonance methods should also be noted in this connection.) Hence, our aim here is to deduce, from the equations given above, and from the continuity conditions

$$\frac{\partial c_i}{\partial t} = - \frac{\partial}{\partial x} (C_i c_i) \quad (4)$$

the generalized form of Fick's second law

$$\frac{\partial c_i}{\partial t} = - \frac{\partial}{\partial x} J_i (c_i B_{ij} \bar{v}_i \phi_{ij} x) \quad (5)$$

where J is the flow. This has to be given in a form suitable for the determination of the diffusion coefficients D from measured diffusion properties, e.g. $c_i = f(x)$, etc. The practical definition and character of such coefficients

$$D = D(c_i B_{ij} \bar{v}_i \phi_{ij}) \quad (6)$$

depends upon the mathematical form of the flows J_i in Eq. (5). As we want to determine the frictions from diffusion data, it is essential to solve the system (6) with respect to frictions:

$$\phi_{ij} = \phi(D c_i B_{ij} \bar{v}_i) \quad (7)$$

This gives the mutual frictions as functions of measurable quantities [cf. Eq. (34)].

III. TWO COMPONENTS

The two-component case provides a good introduction to more complicated cases. From Eqs. (1), (2) and (4), we obtain "Fick's first law" in the form

$$J_1 = - \frac{c_1^2 c_2 \bar{v}_2}{\phi_{12}} RT \left(\frac{\partial \ln a_1}{\partial c_1} \right)_{\xi} \frac{\partial c_1}{\partial x} \quad (8)$$

where $\xi = x, t, p, T$ (ξ is not repeated in the equations which follow).

It is seen that the diffusion coefficient [compare Eq. (6)] is

$$D_{12} = \frac{c_1^2 c_2 \bar{v}_2}{\phi_{12}} RT \frac{\partial \ln a_1}{\partial c_1} \quad (9)$$

Easy transformations show that this D is symmetrical with respect to the components. From the point of view of symmetry, it is most straightforward to express the thermodynamic factor in terms of mole fractions according to Eq. (3):

$$D_{12} = D_{21} = RT X_1 B_{12} / \Phi_2 \quad (10)$$

[$B_{12} = B_{21}$ from the Gibbs-Duhem law $c_1 \partial \ln a_1 + c_2 \partial \ln a_2 = 0$]

where Φ are the molar frictions: $\phi_{12} = \Phi_1 c_1 = \Phi_2 c_2$. In an ideal mixture, $B_{12} = 1$ by definition. If the thermodynamic factor is

expressed by the concentrations c instead of the mole fractions, the diffusion coefficient becomes

$$D_{12} = \frac{RTc_2\bar{v}_2}{\Phi_1} \frac{\partial \ln a_1}{\partial \ln c_1} = \frac{RTc_1\bar{v}_1}{\Phi_2} \frac{\partial \ln a_2}{\partial \ln c_2} \quad (11)$$

Denoting these new derivatives by B_1^c and B_2^c

$$B_2^c/\bar{v}_2 = B_1^c/\bar{v}_1 \quad (\text{Gibbs-Duhem law}) \quad (12)$$

Comparison with Eq. (10) shows that

$$B_{12} = (c_1 + c_2)\bar{v}_2B_1^c = (c_1 + c_2)\bar{v}_1B_2^c \quad (13)$$

The importance of the equations for D_{12} is that they enable us to ascertain the friction coefficients from diffusion measurements. (As some authors prefer to express the results of the measurements in terms of mobilities, we note that the latter would be best defined as $\Omega = 1/\Phi$.) The occurrence of partial volumes in Eqs. (11)–(13) makes the use of the concentrations c less advantageous for practical purposes.

In work on the three-component diffusion theory, the volume fractions $Y (= c\bar{v})$ are found to be the concentration units in which an explicit solution of the problem stated above, i.e. a determination of the friction coefficients from diffusion studies, is possible. Hence, there is a theoretical interest in seeing the analogous treatment for two components. Applying Eq. (4), the flow (8) provides "the second law" of Fick

$$\frac{\partial c_1}{\partial t} = RT \frac{\partial}{\partial x} \left[\frac{c_1^2 c_2 \bar{v}_2}{\phi_{12}} \frac{\partial \ln a_1}{\partial x} \right] \quad (14)$$

Hence, following our intention to refrain from describing diffusion in terms of molar volumes which vary in x and t , $\bar{v}_1$ can be introduced into the derivatives on both sides of (14), giving

$$\frac{\partial Y_1}{\partial t} = RT \frac{\partial}{\partial x} \left[\frac{Y_2}{\Phi_1} \frac{\partial \ln a_1}{\partial \ln Y_1} \frac{\partial Y_1}{\partial x} \right] \quad (15)$$

Substituting

$$B_1^Y = \frac{\partial \ln a_1}{\partial \ln Y_1}; \quad B_2^Y = \frac{\partial \ln a_2}{\partial \ln Y_2} \quad (16)$$

$$B_1^Y/\bar{v}_1 = B_2^Y/\bar{v}_2 \quad (\text{Gibbs-Duhem law})$$

gives

$$\frac{\partial Y_1}{\partial t} = RT \frac{\partial}{\partial x} \left[\frac{Y_2 B_1^Y}{\Phi_1} \frac{\partial Y_1}{\partial x} \right] \quad (17)$$

From this is seen that "Fick's laws" are still valid when volume fractions are used throughout. The diffusion coefficient is given by

$$D_{12}^Y = \frac{RT Y_2 B_1^Y}{\Phi_1} = \frac{RT Y_1 B_2^Y}{\Phi_2} \quad (18)$$

which is different from D_{12} , Eq. (10). It is easy to show that

$$D_{12} = D_{12}^Y \left(1 + \frac{\partial \ln \bar{v}_1}{\partial \ln c_1} \right); \quad \frac{\partial \ln \bar{v}_1}{\partial \ln c_1} = \frac{\partial \ln \bar{v}_2}{\partial \ln c_2} \quad (19)$$

The description in terms of mole fractions *is not this simple*. Starting from Eq. (14), easy calculations give

$$\frac{\partial X_1}{\partial t} = RT (X_1 \bar{v}_1 + X_2 \bar{v}_2)^2 \frac{\partial}{\partial x} \left[\frac{X_2}{(X_1 \bar{v}_1 + X_2 \bar{v}_2)^2} \frac{1}{\Phi_1} \frac{\partial \ln a_1}{\partial \ln X_1} \frac{\partial X_1}{\partial x} \right] \quad (20)$$

Hence, "Fick's law" is strictly valid only if $X_1 \bar{v}_1 + X_2 \bar{v}_2$ is independent of x . As $X_1 + X_2 = 1$, this demands $\bar{v}_1 = \bar{v}_2$. In the case of three components, the tremendous complication arising from $\bar{v}_1 \neq \bar{v}_2 \neq \bar{v}_3$ was observed when using mole fractions for the thermodynamic factors. This was recognized to be a sufficient reason for abandoning a description in terms of mole fractions in this case;¹⁹ see also Section VIII.

IV. THREE COMPONENTS

Profiting by experience already gained we may refrain from details of the calculations for three components (cf. Lamm^{9,19}) and cite (with the volume fractions $Y_1 + Y_2 + Y_3 = 1$) for "Fick's second law"

$$\frac{\partial Y_2}{\partial t} = -RT \frac{\partial}{\partial x} \left[\frac{Y_2}{\sum \phi \phi} \left(\frac{k_{23} Y_3}{\bar{v}_3} \frac{\partial \ln a_3}{\partial x} + \frac{k_{21} Y_1}{\bar{v}_1} \frac{\partial \ln a_1}{\partial x} \right) \right] \quad (21)$$

where

$$\sum \phi \phi = \phi_{12} \phi_{23} + \phi_{23} \phi_{31} + \phi_{31} \phi_{12} \quad (22)$$

and

$$k_{23} = \phi_{31}(Y_3 + Y_1) + \phi_{12} Y_3; \quad k_{21} = \phi_{31}(Y_3 + Y_1) + \phi_{23} Y_1 \quad (23)$$

Characteristic of all these equations and the relevant equations below is the *cyclic permutation* $1 \rightarrow 2 \rightarrow 3 \rightarrow 1$ connected with the symmetric treatment of the components.

It is essential to resolve the x -derivatives of the activities occurring in Eq. (21) into specific thermodynamic coefficients B multiplied by x -derivatives of the concentrations Y . The B -values are defined* as

$$B_{23}^Y = \left(\frac{\partial \ln a_2}{\partial \ln Y_2} \right)_{Y_3}; \quad B_{21}^Y = \left(\frac{\partial \ln a_2}{\partial \ln Y_2} \right)_{Y_1} \quad (24)$$

A simplification is accomplished by using E -coefficients:

$$E_{ij} = B_{ij}^Y / \bar{v}_i \quad (25)$$

Applying the Gibbs–Duhem relation $\sum (Y_i / \bar{v}_i) d \ln a_i = 0$ shows that they are connected by

$$E_{23} + E_{32} = E_{31} + E_{13} = E_{12} + E_{21} \quad (26)$$

and, as Ljunggren²² has been able to show, the cross-differential relations

$$\frac{\partial \mu_i(n_1 n_2 n_3)}{\partial n_j} = \frac{\partial \mu_j(n_1 n_2 n_3)}{\partial n_i}$$

(where n is the number of moles) lead to the further relationship

$$\frac{E_{12}}{Y_1} + \frac{E_{23}}{Y_2} + \frac{E_{31}}{Y_3} = \frac{E_{13}}{Y_1} + \frac{E_{21}}{Y_2} + \frac{E_{32}}{Y_3} \quad (27)$$

Hence, with six coefficients and three independent relationships between them, the number of independent thermodynamic magnitudes to consider in three-component diffusion is only three.

The $\ln a_i$ of Eq. (21) are functions of two independent volume fractions and $\sum dY_i = 0$. The equation can be reduced to a form suitable for the definition of the six diffusion coefficients D_{ij}^Y for three-component diffusion. Omitting the superscript in these D^Y coefficients, the result of the calculation¹⁹ is

$$\frac{\partial Y_2}{\partial t} = - \frac{\partial}{\partial x} \left[D_{23} \frac{\partial Y_3}{\partial x} + D_{21} \frac{\partial Y_1}{\partial x} \right] \quad (28)$$

* In view of Eq. (3), the B 's of Eq. (24) would have to change indice, the first being 21 and the second 23. In order to avoid confusion with earlier publications, we do not make this change, which is of no importance as long as the number of components is lower than 4.

where

$$\begin{aligned} D_{23} &= \frac{RTY_2}{\sum \phi\phi} [k_{21}(E_{13} - E_{12}) + k_{23}E_{31}] \\ D_{21} &= \frac{RTY_2}{\sum \phi\phi} [k_{23}(E_{31} - E_{32}) + k_{21}E_{13}] \end{aligned} \quad (29)$$

and

$$D_{23} + D_{13} = D_{31} + D_{21} = D_{12} + D_{32} \quad (30)$$

The subjective element in the procedure which leads to the definitions of these D_{ij} is small, if we stick to demands of symmetry and simplicity. In view of the relations (23), only arithmetic is required to reach the goal of the theory, viz., to express the frictions ϕ in terms of measurable quantities. A considerable arithmetic advantage is gained if we define the D_i 's as

$$D_2 = \frac{D_{31}}{Y_3} + \frac{D_{13}}{Y_1} = \frac{RT}{\sum \phi\phi} (\phi_{12}E_{32} + \phi_{23}E_{12}) \quad (31)$$

and the Δ_i 's as

$$\Delta_2 = \phi_{31} \frac{RT}{\sum \phi\phi} = \frac{D_3E_{31}E_{12} + D_1E_{32}E_{13} - D_2E_{31}E_{13}}{E_{12}E_{23}E_{31} + E_{21}E_{32}E_{13}} \quad (32)$$

because then the quadratic friction sum, which has remained unsolved ever since it appeared in Eq. (21), is simply

$$\begin{aligned} \sum \phi\phi &= (RT)^2 / \sum \Delta\Delta \\ \sum \Delta\Delta &= \Delta_1\Delta_2 + \Delta_2\Delta_3 + \Delta_3\Delta_1 \end{aligned} \quad (33)$$

When this is introduced into Eq. (32) we obtain by analogy with the Nernst-Einstein relation $\Phi = RT/D$

$$\phi_{31} = RT\Delta_2 / \sum \Delta\Delta \quad (34)$$

Evidently, $\phi_{31}/\Delta_2 = \phi_{12}/\Delta_3 = \phi_{23}/\Delta_1$. By diffusion, thermodynamic, and partial volume measurements, the Δ_i can be ascertained experimentally from the definition of D_i and the expressions for Δ_i given in Eq. (32).

The algebraic simplicity of

$$\frac{D_{12}}{Y_1} + \frac{D_{23}}{Y_2} + \frac{D_{31}}{Y_3} = \frac{RT}{\sum \phi \phi} (\phi_{12}E_{32} + \phi_{23}E_{13} + \phi_{31}E_{21})$$

(35)

or

$$\frac{D_{21}}{Y_2} + \frac{D_{32}}{Y_3} + \frac{D_{13}}{Y_1} = \frac{RT}{\sum \phi \phi} (\phi_{12}E_{31} + \phi_{23}E_{12} + \phi_{31}E_{23})$$

is also of interest because, eliminating the frictions $\phi/\sum \phi \phi$ by the use of Eq. (32) and considering our relations (26), the following expression is easily deduced:

$$\frac{D_{12}E_{12}}{Y_1} + \frac{D_{23}E_{23}}{Y_2} + \frac{D_{31}E_{31}}{Y_3} = \frac{D_{21}E_{21}}{Y_2} + \frac{D_{32}E_{32}}{Y_3} + \frac{D_{13}E_{13}}{Y_1} \quad (36)$$

Although the point of departure is not symmetrical [only one of the equations (35) is needed], the result (36) is symmetrical, and it is also unique. It does not contain frictions. It represents an equation whose experimental verification has a meaning analogous to the interesting (and difficult) experimental verification of the Onsager reciprocal relation, with which works by Fujita and Gosting,³ and Miller *et al.*^{23,24,30} on three-component diffusion are concerned. The author prefers to look upon Eq. (36) as a means of facilitating the exact computation of frictions (numerical equalization and the testing of data), and of procuring thermodynamic data from diffusion measurements, although these are not easily obtained. The works cited are theoretically based upon the reciprocity relations of irreversible thermodynamics. The equivalence of the dynamic treatment reviewed here with the latter approach to the problem has been elucidated in detail by Ljunggren,²² as already mentioned in the introduction.

From Eqs. (30) and (36) we see that three-component diffusion is regulated by three independent diffusion coefficients. Hence, as far as D_{ij} , E_{ij} and ϕ_{ij} ($\phi_{ij} = \phi_{ji}$) are concerned, the general problem includes three independent coefficients of each kind.

In a fairly recent article, Truesdell³³ scrutinizes the foundations of the different theories of diffusion from very general points of departure, thereby casting doubts upon the validity of the reciprocity and symmetry relations used. This criticism also concerns

our relations $\phi_{ij} = \phi_{ji}$ ($k > 2$), Eq. (1). Quantitative estimations are still lacking.

In view of this, an experimental test of Eq. (36) becomes of enhanced importance. However, an easier way to obtain results of high accuracy would eventually be to measure the *electrical* properties of a non-solvated electrolyte in a concentration gradient formed by a mixed solvent.

From an *experimental point of view*, it is necessary to determine the coefficients of Eq. (28) (and of the two similar equations obtained by cyclic permutation) from measured concentration functions. As the partial volumes are assumed to be independent of x and t , we also have

$$\frac{\partial c_2}{\partial t} = - \frac{\partial}{\partial x} \left[D_{23}^c \frac{\partial c_3}{\partial x} + D_{21}^c \frac{\partial c_1}{\partial x} \right] \quad (37)$$

In a real differential measurement, the diffusion coefficients are constant:

$$\frac{\partial c_2}{\partial t} = - \left[D_{23}^c \frac{\partial^2 c_3}{\partial x^2} + D_{21}^c \frac{\partial^2 c_1}{\partial x^2} \right] \quad (38)$$

This type of differential equation was treated mathematically by Fujita and Gosting.³ From Eq. (28) it is evident that the transformation from D^c to D is simple:

$$D_{ij} = D_{ij}^c \frac{\bar{v}_i}{\bar{v}_j} \quad (39)$$

In contradistinction to this simplicity, the transformation of thermodynamic factors between different concentration units (X, c, Y) is complicated, in as far as the partial volumes cannot be regarded as independent of the *concentrations*. The thermodynamic factors E_{ij} cannot be determined exactly without the use of concentration derivatives of partial volumes (eventually by a graphical procedure) [compare Eq. (19) for only two components].

In an ideal mixture, the partial volumes are independent of composition, and all the B^X [Eq. (3)] are unity. When volume

fractions are used [Eqs. (24), (25)], this simple picture no longer holds, and instead (Ljunggren, unpublished)

$$B_{ij}^Y \rightarrow 1 + X_i \left(\frac{\bar{v}_i}{\bar{v}_l} - 1 \right) \quad (40)$$

the three components being i , j and l .

This follows from

$$B_{ij}^Y \rightarrow \left(\frac{\partial \ln X_i}{\partial \ln Y_i} \right)_{Y_j} \quad (\text{all } B^X = 1) \quad (41)$$

use being made of the fact already mentioned that all the $\bar{v}$'s are independent of concentration in an ideal mixture.

V. REDUCTIONS TO SELF DIFFUSION

Molar frictions may generally be defined as $\Phi_{ij} = \phi_{ij}/c_i$. This magnitude is the friction between the components i and j in a volume containing one mole of component i . The resistivity, $R_{ij} = \phi_{ij}/c_i c_j$, is also of interest. It occurs (with opposite sign) in Onsager's²⁶ theory of multicomponent diffusion. The symmetry of ϕ_{ij} immediately leads to the symmetry of R_{ij} (compare Lamm¹⁸) and *vice versa*. Other aspects of the topic have been studied by Laity⁸ and Ljunggren.²²

Our equation (10) for two components shows that the diffusion coefficient may be written as

$$D_{12} = RT \frac{c_1 c_2}{c_1 + c_2} \frac{B_{12}}{\phi_{12}} \quad (42)$$

Assuming the components to be *identical*, $B_{12} = 1$ and $c_1 + c_2 = 1/v = \text{a constant}$ ($\bar{v}_1 = \bar{v}_2 = v$). It is a statistical necessity that D_{12} is independent of the mixing ratio, proving that the resistivity $\phi_{12}/c_1 c_2 = R_{12}$ is constant for self diffusion.

Analogous considerations are valid for three-component diffusion (Lamm^{10,15}). In the self diffusion of three identical components, the diffusion coefficients reduce to one single coefficient D_{123} , which is independent of the mixing ratios:

$$D_{123}/RTv = c_1 c_2 / \phi_{12} = c_2 c_3 / \phi_{23} = c_3 c_1 / \phi_{31} = 1/R_{123} \quad (43)$$

($\bar{v}_1 = \bar{v}_2 = \bar{v}_3 = v$). We cannot easily deduce these relations from Eq. (29): only mole fractions are suitable concentrations for this purpose. All the B^x are unity in an ideal mixture and, as a matter of course, also in an identical mixture.

General three-component diffusion equations may be reduced in two ways to concern only two chemically different components. One of these ways leads to the ordinary two-component equation presented above. The other leads to equations for self diffusion of a component in a mixture with a second component (Lamm^{13,14,15}). The former component is split in two parts, (ideally) labelled by the isotope tracer procedure, which form a diffusion gradient. The latter component is assumed to have a constant concentration during the self-diffusion experiment (the more general case is of minor interest). We will mainly reproduce here the result which has a bearing upon the (relative) constancy of the resistivities.* Let the chemically different components be a and b . The former is composed of two isotopically different, but with respect to diffusion properties identical, substances (a)1 and (a)2: $c_a = c_1 + c_2$. In view of what has been stated above regarding resistivities, it is natural to assume, as an approximation, that

$$R_{12} = \phi_{12}/c_1c_2 = \text{constant } [\neq f(c_b)] \quad (44)$$

This equation transposes the "law of mass action" into the field of resistivities.

The ordinary diffusion coefficient [see Eq. (42)] in this case is

$$D_{ab} = RTB_{ab}c_ac_b/\phi_{ab}(c_a + c_b) \quad (45)$$

By calculations, not reproduced here,¹³ the reduction of the three-component kinematics to the case described leads (without approximations) to

$$\frac{RT}{D_{12}} = \phi_{12} \left(\frac{1}{c_1} + \frac{1}{c_2} \right) + \phi_{ab} \frac{1}{c_1 + c_2} \quad (46)$$

* In its applicability to self diffusion and to gaseous systems, the tendency of the resistivities to be constant was first observed by Ljunggren.²² In condensed systems in general, the conditions are more complicated, as shown for example by the usefulness of Stokes' law for molar frictions.

where D_{12} is the coefficient of self diffusion of a in the mixture. If the assumed independence of R_{12} on c_b is correct, R_{12} will have the same value as in the pure component a ; hence, according to (42)

$$R_{12} = \frac{\phi_{12}}{c_1 c_2} = \frac{RT v_a^0}{D_{12}^0} \quad (47)$$

where D_{12}^0 and v_a^0 are the self-diffusion coefficient and the molar volume of the pure component a , respectively. Eliminating the frictions in (46) through the expressions (45) and (47), we obtain

$$\frac{1}{D_{12}} - \frac{c_a v_a^0}{D_{12}^0} = \frac{B_{ab} X_b}{D_{ab}} \quad (48a)$$

where c is the concentration and X the mole fraction. The measurements of Johnson and Babb^{6,7} gave the result expected on these theoretical grounds. Equation (48a) is approximately valid for a normal fluid component in a mixture with another normal component or with an associated liquid. It was found not to be valid for the self diffusion of an associated component mixed with a normal liquid; Eq. (48a) entirely disregards effects such as the specific dissolution of association, which results from the dilution with the normal component. Except for complications of the latter kind, the resistivity (44) seems to be approximately constant. Further experiments of this kind can hardly fail to throw light upon the nature of the *liquid state*. This is also true of diffusion studies starting from other points (compare for instance Hildebrand *et al.*²⁹ and Irani and Adamson⁵).

There is no reason why there should be no general "medium effect" upon the resistivities. The approximate nature of Eqs. (44) and (48a) gives rise to speculations regarding their improvement, which however do not belong to the field of macro-dynamics. The self diffusion of a medium containing solvated macro-molecules was studied by Wang.²⁸

It will be useful to define resistivity interaction parameters ρ_a (and ρ_b) according to $R_{12} = RT v_a^0 \rho_a / D_{12}^0$, which may be measured by

$$\rho_a = \frac{D_{12}^0}{c_a v_a^0} \left(\frac{1}{D_{12}} - \frac{B_{ab} X_b}{D_{ab}} \right) \quad (48b)$$

We calculated R_{12} from the self diffusion of *pure a*, Eq. (47). The *opposite* case, $c_a \rightarrow 0$, leads in Eq. (48a) to $B_{ab} = 1$ and $X_b = 1$, hence $D_{12} \rightarrow D_{ab}$, which is experimentally verifiable and self-evident.

Reduced to the self diffusion of an ideal gas mixture, Eq. (48a) assumes the form

$$\frac{p}{D_{12}} = \frac{p_a}{D_{12}^0} + \frac{p_b}{D_{ab}} \quad (p = p_a + p_b) \quad (49)$$

where p_a, p_b are the partial pressures of *a* and *b*. It describes, for instance, the self diffusion, D_{12} , of nitrogen (*a*) in oxygen (*b*). C. F. Curtiss communicated to the author that Eq. (49) may be deduced from D. Enskog's treatment of gas diffusion. Further applications to the ordinary kinetic gas theory, and to the electron gas theory, were successfully made by Ljunggren,²² through calculations of R_{12} on the basis of molecular kinetics.

The preliminaries to Eqs. (48) contain the following (exact) expression for the coefficient of self diffusion D_{12} [identical with Eq. (46)]:

$$D_{12} = RT/(\Phi_{1(2)} + \Phi_{2(1)} + \Phi_{a(b)}) \quad (50)$$

where $\Phi_{1(2)} = \phi_{12}/c_1$ and $\Phi_{2(1)} = \phi_{12}/c_2$ are the molar frictions between the identically labelled parts of component *a*, and $\Phi_{a(b)}$ is the molar friction of component *a* as a whole, against component *b*. The mutual diffusion coefficient, Eq. (45), may be rewritten by analogy with Eq. (10)

$$D_{ab} = \frac{RTB_{ab}X_b}{\Phi_{a(b)}} = \frac{RTB_{ab}}{\Phi_{a(b)} + \Phi_{b(a)}} \quad (51)$$

These two equations, (50) and (51), illustrate how the macrodynamic theory can give a kinematic framework, which may be of interest in connection with work on the *molecular* dynamics of diffusion. It is seen that on a fundamental basis it is not possible to express the mutual coefficient D_{ab} in terms of the two self-diffusion coefficients D_{12}^a (of component *a*) and D_{12}^b (of component *b*). As a matter of fact, self diffusion of a component in a mixture is a more *complicated* process than mutual diffusion, as far as frictions are concerned, because according to (50) it depends on two kinds of friction, viz., internal friction within this component

and external friction against the other component. (This is simply a consequence of the fact that self diffusion in a mixture is a three-component case, whereas the mutual process is a two-component diffusion.) In other respects, the self diffusion is *simpler*, e.g. with regard to the partial volumes ($\bar{v}_1 = \bar{v}_2$) and the thermodynamics ($B = 1$).

VI. DETAILS REGARDING THE CHEMICAL COMPONENTS AS DYNAMICAL OBJECTS

Classical thermodynamics and theories of state equilibrium show an admirable flexibility with regard to the choice of components; primarily only the number of these is essential. This advantage has been taken over by the diffusion theory with the thermodynamic factor as an intermediate link. As a consequence, it must be admitted that the molar frictions contained in the theory (ϕ_{ij}/c_i) do not necessarily correspond to the frictional coefficients of the special molecular species contained in the mixture. So that the latter shall be the case, a component must consist of only one kind of molecule, and (in calculating the molar properties contained in the theory) the molecular weight of the component must be chosen according to the actual molecular species.

Articles by the present writer^{10,12,16} and by Ljunggren²¹ are concerned with the thermodynamics and frictional properties of components consisting of a number of molecular species in rapid equilibrium with one another. One result is a simple law which is valid for the molar friction of a binary system, e.g. Φ'' of component 2, expressed in terms of the frictions of the different molecular species of this component. Assume that the molecular weight of the component is chosen to be M , corresponding to simple molecules with the chemical symbol A. Other molecules in equilibrium with A are A_n ($n = 2, \dots$) with frictions Φ_n'' . In the actual solution, the fraction of the component which exists as A_n is written γ_n'' . It is easily shown that the inverse of the *component* friction Φ'' is given by

$$\frac{1}{\Phi''} = \sum_n \frac{n\gamma_n''}{\Phi_n''}; \quad \sum \gamma_n'' = 1 \quad (n = 1, 2, \dots) \quad (52)$$

So, for instance, if the component consists entirely of double molecules, $\gamma_1'' = 0$, $\gamma_2'' = 1$. Hence, from (52), $\Phi_2'' = 2\Phi''$. (Φ'' is the magnitude calculated from a diffusion experiment, whereas Φ_2'' divided by Avogadro's number is the real molecular friction in our example.)

A further example of the flexibility of Eq. (10) is that in the thermodynamic factor $B_{12} = 1 + \partial \ln f_2 / \partial \ln X_2$, the activity coefficient of the *component* 2, f_2 , differs from unity not only because of intermolecular forces, but also owing to *ideal* dissociation and association.^{10,12,13}

Thus, on the assumption that the different molecular species A_n in equilibrium with one another are ideal and dilute, the following simple relation holds for the thermodynamic factor in Eq. (10) (more general relations for B_{12} are deduced in Reference 12):

$$B = 1 + \frac{\partial \ln \gamma_1''}{\partial \ln C''} = \frac{1}{n} \left(1 + \frac{\partial \ln \gamma_n''}{\partial \ln C''} \right) \quad (53)$$

where C'' is the total concentration of component 2 in mole cm^{-3} , calculated with the molecular weight of the simple molecule A. From Eq. (10), with $X_1 = 1$, we obtain

$$D'' = RT \left(1 + \frac{\partial \ln \gamma_1''}{\partial \ln C''} \right) \sum \frac{n\gamma_n''}{\Phi_n''} \quad (54)$$

In some cases, e.g. of weak association, it may become a matter of convention what shall be regarded as the formation of new (associated) molecules, and what we wish to describe merely as a field of force existing between simpler molecules. Such considerations lead to the theory of the fluid states.

Diffusion and sedimentation theories can, like thermodynamics, be formulated without using the molecular concept; at the same time, however, they will eventually lose some of their inherent value. As an example, Eq. (9) is written without reference to molar properties. We have

$$RT \frac{\partial \ln a_1}{\partial \ln c_1} = c_1 \frac{\partial \mu_1}{\partial c_1} = m_1 M_1 \frac{\partial g_1}{\partial m_1} \quad (55)$$

where m is the concentration in g/cm³ and g is the chemical potential per gram. Hence,

$$D_{12} = \frac{m_1^2 m_2 \bar{V}_2}{\phi_{12}} \frac{\partial g_1}{\partial m_1} = \frac{m_2^2 m_1 \bar{V}_1}{\phi_{12}} \frac{\partial g_2}{\partial m_2} \quad (56)$$

(V is the partial specific volume), considering $\sum \bar{V}_i dm_i = 0$ and $\sum m_i dg_i = 0$. Whenever *molar* properties are introduced, it is necessary to stick to the assumed *component* molecular weights throughout a calculation.

Let the components be A' and A'' , of molecular weights M' and M'' , and the concentrations c' ($= m_1/M'$) and c'' ($= m_2/M''$) mole/cm³. Another choice of components may be denoted most generally by $A'_{r_1} A''_{s_1}$ and $A''_{r_2} A'_{s_2}$. This allows for compound formation between the two substances ($s \neq 0$), as well as for association ($r \neq 1$). The diffusion coefficient is invariant with these two alternative choices of components, the actual mixture being the same in the two cases. This invariance condition leads to¹⁶

$$\frac{\phi_{12}^*}{\phi_{12}} = \left[\frac{(c_1 s_1 - c_2 r_1)(c_1 r_2 - c_2 s_2)}{c_1 c_2 (r_1 r_2 - s_1 s_2)} \right]^2 \quad (57)$$

ϕ_{12} is the friction per cm³ for the first choice and ϕ_{12}^* for the second choice of components. The same transformation from ϕ_{12} to ϕ_{12}^* was calculated from the sedimentation theory,²⁰ which is simpler to carry out as the thermodynamic factor is not included in the latter process. It is seen from Eq. (57) that simple multiples of components ($s_1 = s_2 = 0$), for instance I_2 instead of I and N_2O_4 instead of NO_2 , does not affect ϕ_{12} ($\phi_{12} = \phi_{12}^*$). The transformation is of a formal nature, and its origin is the actual freedom as to the choice of components of a given system already referred to. However, if a calculation of the molar friction from diffusion experiments has been carried out with components which do not correspond to the actual molecular constituents of the mixture, the condition (57) can be used in a simple way to obtain the friction of an actual molecule, e.g. I_2 , if it is known from other measurements that practically the only form in which iodine is present is as double molecules.

The developments described above have been made on the assumption of a "mechanically normal" fluid behaviour. This does not mean that the flow properties must be Newtonian. The vital point is that the dissipation of free energy is described simply as a pure frictional process *between* the components. (That this is consistent with the optional choice of components, e.g. according to the scheme of Eq. (57), is an interesting fact, not immediately intelligible.) Accordingly, Eq. (9) or (10) can be obtained by equating the frictional dissipation of free energy with the available free energy of mixing.³¹

The question of a mechanically normal behaviour has an analogous bearing upon the range of validity of the linear phenomenological flow equations of irreversible thermodynamics. Somewhere between a normal fluid and a gel there must exist systems which are still fluid but where an elastic relaxation dissipation process invalidates the main assumptions used in both approaches, or makes them incomplete. In such systems, "Fick's laws" may no longer be valid.³¹

What has just been stated does not prevent the application of the theories to systems which contain a really rigid structure, e.g. a zeolitic structure or a solid membrane,^{31,32} as part of the system. With simple modifications, especially the introduction of friction coefficients between the fluid components and the structure, a theoretical interpretation along the lines of macro-dynamics would not fail to afford tangible results (see Reference 31).

VII. A CASE OF NON-DIFFERENTIAL THREE-COMPONENT DIFFUSION

The planning of experiments on three-component diffusion for the determination of diffusion coefficients and frictions, in a way which makes full use of the available instrumental accuracy, is a question of considerable complexity. There are three main types of experiment to consider, viz., two components are dilute (e.g. 1 and 3), one is dilute (e.g. 2), or none is dilute. The latter requires the full equations reported above. The first case is of interest as it enables us to determine the special flow interaction between two components which arises at low concentrations of the components, and which is therefore simplest to interpret

theoretically. This non-thermodynamic interaction is adequately expressed by the friction coefficient ϕ_{13} or the resistivity ϕ_{13}/c_1c_3 . The intermediate type mentioned represents the diffusion of a dilute substance (micro-component) in a mixed medium. Of especial interest is the diffusion which is caused by a gradient in the macro-components 1 and 3. This phenomenon has been called the *Arrhenius-Thovert effect*. For this effect to be pronounced, the gradient cannot be small, and we no longer have differential diffusion.

Leaving out of consideration effects due to a volumetrically non-ideal behaviour, the Arrhenius-Thovert effect may be calculated, for example, from Eqs. (21)–(24), and (5). If $Y_2 \ll Y_1$, Y_3 and $\phi_{12}, \phi_{23} \ll \phi_{31}$, we observe that $k_{21} = k_{23} = \phi_{31}(Y_3 + Y_1)$. Hence, for the flow

$$J_2 = - \frac{RTc_2}{\Phi_2} \frac{\partial \ln a_2}{\partial x}, \quad (58)$$

$$\Phi_2 = \frac{\phi_{12}}{c_2} + \frac{\phi_{23}}{c_2} = \Phi_{2(1)} + \Phi_{2(3)}$$

This equation can also be obtained directly from a macrodynamical starting point: $C_2 = -(1/\Phi_2)\partial\mu_2/\partial x$ for the velocity $C_2 = J_2/c_2$, although there may be some doubt as to the additive nature of the frictions in the latter simple mode of procedure.*

From Eq. (58) it is seen that the flow is regulated by the potential gradient, and that a thermodynamic knowledge of the system is needed for further penetration of the effect. In the case of an ideal thermodynamic behaviour, $a_2 = X_2$; analogous approximations ($c_2 \ll c_1, c_3$ and $\bar{v}_2 \partial c_2/\partial x \ll \bar{v}_1 \partial c_1/\partial x, \bar{v}_3 \partial c_3/\partial x$) easily give

$$J_2 = - \frac{RT}{\Phi_2} \left(\frac{\partial c_2}{\partial x} - \frac{X_2(\bar{v}_3 - \bar{v}_1)}{\bar{v}_3} \frac{\partial c_1}{\partial x} \right) \quad (59)$$

where J_2 is the flow of the micro-component for the case of a strong gradient of the macro-components.

The first term within the brackets describes the “normal” diffusion of component 2. For an Arrhenius-Thovert effect to

* At infinite dilution ($a_2 = c_2$), Eq. (58) presents Fick’s law in the traditional form. In this respect, there is no difference between diffusion in a pure medium and diffusion in a mixture.

occur in our approximation, the molar volumes of the macro-components must be different. This flow is directed towards increasing concentration of the component with a smaller molar volume: a purely thermodynamic necessity.

In order to get a quantitative description of an easily realized experiment, we may assume a sharp boundary between the macro-components at x , $t = 0$, and a constant concentration of the micro-component all over the cell. As the latter substance 2 will have a vanishingly small influence upon the diffusion of 1 and 3, we obtain the well known Gaussian x -dependence of $\partial c_1 / \partial x$:

$$\frac{\partial c_1}{\partial x} = \frac{c_1'' - c_1'}{2\sqrt{(\pi D_{13}t)}} \exp\left(-\frac{x^2}{4D_{13}t}\right) \quad (60)$$

where D_{13} is the diffusion coefficient of the macro-components 1 and 3, and c_1' and c_1'' are the original boundary concentrations of component 1. Hence, for the flow through the level $x = 0$, according to Eq. (59),

$$J_2 = -\frac{RT}{\Phi_2} \left(\frac{\partial c_2}{\partial x} - A \frac{c_2}{\sqrt{t}} \right) \quad (61)$$

$$A = \frac{(\bar{v}_3 - \bar{v}_1)(c_1'' - c_1')}{2[1 + c_1(\bar{v}_3 - \bar{v}_1)]\sqrt{(\pi D_{13})}}$$

The Fickian term is zero at $t = 0$. Thus, for short diffusion times, the flow in each experiment is mainly regulated by

$$J_2 = \frac{c_2(c_1'' - c_1')}{\sqrt{t}} \cdot \text{const.} \quad (62)$$

The full differential equation which describes $c_2 = f(x, t)$ is

$$\frac{\partial c_2}{\partial t} = RT \frac{\partial}{\partial x} \left\{ \frac{1}{\Phi_2} \left[\frac{\partial c_2}{\partial x} - A \frac{c_2}{\sqrt{t}} \exp\left(-\frac{x^2}{4D_{13}t}\right) \right] \right\} \quad (63)$$

For less simple cases than the one described, no methods of approximation have been worked out. The circumstance that one or two components are supposed to be very dilute will mainly be a simplification from thermodynamic aspects, and as regards the mathematical solution of Eqs. (38).

VIII. HISTORICAL REMARK ON THE OSMOTIC PRESSURE AND DIFFUSION

The use of the macro-dynamical method previously in connection with the osmotic theory of force [the diffusion of electrolytes and ionic mobilities by Nernst; diffusion and the hydrodynamic (Stokes') radius of molecules according to W. Sutherland and Einstein] is well known. An alternative, simple formulation of two-component diffusion, Eq. (10), is possible if another form of the thermodynamic factor, based upon osmotic pressure P ,^{12,14} is applied:

$$-Q_{12} = c_1 \frac{\partial P_2}{\partial c_1} = c_2 \frac{\partial P_1}{\partial c_2} \quad (\text{Gibbs-Duhem law}) \quad (64)$$

viz.,

$$D_{12} = Y_1 Y_2 Q_{12} / \phi_{12} = \bar{v}_1 \bar{v}_2 Q_{12} / R_{12} \quad (65)$$

The differential osmotic pressure factor $Q_{12} = Q_{21}$ does not seem to have been used in other connections. This factor is of interest here owing to the physical foundation it gives to the use of E -factors, defined in Eq. (25). From Eqs. (15), (16), and (24), it appears that Q_{12}/RT is identical with the E -factor corresponding to a two-component case:

$$\frac{Q_{12}}{RT} = \frac{1}{\bar{v}_1} \frac{d \ln a_1}{d \ln Y_1} = E_1 = E_2$$

The osmotic pressure theory for three components has not been worked out from the points of views guiding the present article.

The author is greatly indebted to Mr. Stig Ljunggren, tekn.lic., for having read the manuscript.

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MANY-ELECTRON THEORY OF ATOMS, MOLECULES AND THEIR INTERACTIONS*

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* Work supported by a grant from the National Science Foundation.

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I. INTRODUCTION

This article is concerned with the calculation of the wave functions and energies of many-electron atoms and molecules. The properties of primary interest are: (*i*) total energies, ionization potentials, electronic spectra, and dissociation energies of molecules, (*ii*) heats of formation, isomerization and conformational changes of large molecules, and (*iii*) intermolecular forces over all ranges of separations. Although not directly dealt with, the calculation of other properties such as polarizabilities, magnetic shielding, etc., can also be improved by the use of the wave functions of the theory.

Most of the properties listed require a high degree of accuracy because they involve small energy differences between large quantities. A theory useful for chemistry must be sufficiently accurate but also deal in a simple way with a large variety of molecules which have similar groups. We therefore consider both semi- and non-empirical schemes. The objective is to make

use of "chemical" simplifications in non-empirical "molecular quantum mechanics" (but not in an *ad hoc* fashion), and also to have a quantitative basis for a semi-empirical "quantum chemistry".

II. WHY A "MANY-ELECTRON" THEORY?

Quantum chemistry is based on orbitals: The Heitler–London (H.L.) or the molecular orbital (MO) methods. These two methods are comparable as starting points and, if corrections are carried far enough, equivalent. The Heitler–London method has turned out to be cumbersome for large molecules, especially for the theory of spectra. The best molecular orbitals are those given by the Hartree–Fock (H.F.) method,¹ which gives an equation for the orbit of each electron in the self-consistent average field of all the other electrons. We shall take H.F. MO's, or approximations to them such as LCAO MO's, as the starting point. This makes the theory of remaining effects simplest.

Orbitals do not consider the instantaneous repulsions, the "collisions", between electrons. The resulting error, i.e. "the difference between the exact non-relativistic energy and the Hartree–Fock energy" of a many-electron system is defined as the "correlation energy".¹ As emphasized by Löwdin¹ and Pitzer,² these errors are comparable in magnitude to the energy quantities of interest. It appears, therefore, that we may have to deal with a complicated many-electron problem and abandon the orbitals approach. But the situation is not as bad as it may seem at first sight for two reasons. First, not all properties, e.g. charge distributions, are as strongly affected by correlation as energy differences. Secondly, the exclusion principle and the nuclear framework ensure that mainly two electrons "collide" at a time in spite of the long range of Coulomb repulsions. The "many-electron" problem is then really a series of few-electron problems.

Electron correlation is responsible for the following effects:

(1) An error of *ca.* 1 to 2 eV per doubly occupied Hartree–Fock orbital, e.g. in $\text{He } 1s^2$ -1.142 eV,¹ in H_2 (interatomic distance, $r = r_e$) -1.06 eV,¹ and in the $(2p_z)^2$ pair of Ne *ca.* -1.6 eV.⁶⁹ The relative error is comparable to the binding energy in N_2 for example (see Section XXV).

(2) "Core polarization"³ by valence electrons; e.g. a π -electron instantaneously polarizes the sigma core; similarly "series" levels shift in alkali spectra. This (1s)(2s) correlation in lithium is *ca.* -0.05 ev.⁴

(3) The potential curve of the H_2 molecule is in error¹ by 7.74 ev at dissociation if the Hartree-Fock $(1\sigma_g)^2$ is used at all internuclear distances, r . Most molecules dissociate into the wrong states if one continues to apply the H.F. method to the same electronic configuration at large r as near the equilibrium value r_e (see for example also N_2 ; Reference 5).

(4) Often in electronic spectra, e.g. where Hund's rules hold, H.F. MO's give the correct level scheme. Each level, however, is shifted by correlation errors as in case (1) above ("adiabatic" level shifts).

(5) Near-degeneracy or "resonance" between configurations may change the H.F. level scheme as in the breakdown of Hund's rules, e.g. in the (3s3d) levels⁴⁴ of Mg. These "non-adiabatic" level changes are due to "first-order configuration-interaction" (C.I.) effects.⁶ Effect (3) is also of this type.

(6) The London-dispersion-type Van der Waals attraction between, say, two argon atoms or between two ends of *n*-butane is strictly a correlation effect.² Such interactions are of the order of 10^{-3} ev. Correlations between different shells of an atom or molecule [effect (2) above] may also be viewed³ as "Van der Waals" attractions.

(7) In metals and highly conjugated dye molecules many electrons correlate at once and behave as an "electron gas" with collective screening and oscillation effects.⁷

(8) A question important in justifying the use of orbitals alone in qualitative quantum chemistry is: will correlation modify the H.F. orbitals? i.e. are there orbitals which represent a larger portion of the exact wave function (w.f.) than H.F. MO's do?

The effects listed above necessitate the study of electron correlation.

Löwdin¹ has reviewed the state of the theory up to 1959 stressing the methods that give high accuracy for two-electron systems. Pitzer² has dealt with correlation between non-overlapping shells of electrons, and with the semi-empirical evaluation

of inter- and intra-molecular London–Van der Waals attractions. This review gives the “many-electron theory” developed over the past few years.^{8–10} Related approaches are discussed as they come up.

A preliminary look at conventional semi- and non-empirical schemes will clarify the objectives and the reasons for the particular lines of attack taken by the “many-electron theory”.

III. SEMI-EMPIRICAL THEORIES

Semi-empirical theories of electronic spectra are based on orbitals (Hartree–Fock or approximations to them). In both atomic and π -electron spectra, cores and instantaneous “core-polarizations” by outer electrons are omitted. For π -electrons it is customary to assume an empirical “ Π -electron Hamiltonian”^{11,12} H_{Π} which depends on the static field of the sigma core assumed unchanged for different electronic states.

The energy expressions given by these orbital theories are parametrized. In atomic spectra, F and G integrals,¹³ and in the Π -electron case α , β and one and two center Coulomb integrals are left as semi-empirical parameters. Empirical values of these integrals give quite good agreement with experiment, but such agreement is lost if the parameters are actually calculated from orbitals. Empirical values evidently include electron correlation.^{12,14,15}

Relative energies of saturated molecules are also calculated well semi-empirically if constant bond energies are assumed and zero point vibrations and London–Van der Waals attractions between non-bonded regions are considered.² In this way, the heats of formation and isomerization of saturated hydrocarbons are obtained to within² 0.01 ev or 0.2 kcal/mole.

The common feature of these schemes is the assumed separability of certain groups of electrons, inner–outer shells, bonds, etc., and their invariance from one atom or molecule to another. These assumptions are valid (see below) for the orbital pictures as such, but must be justified for the correlation part. Semi-empirical theories ought to be based on a theory which includes electron correlation at the outset and then does the parametrization in a well defined fashion.

IV. NON-EMPIRICAL THEORIES

An exact many-electron wave function can be expanded in an infinite series of all the "ordered" Slater determinants that can be formed from a one-electron basis set. Usually calculations on systems of more than two electrons are made by taking a finite number of such configurations as a linear trial function [configuration-interaction (C.I.) method¹]. The expanded form of the ordinary perturbation theory may also be considered an approximate way of doing C.I.^{1,16}

C.I. is suitable for the removal of actual or near degeneracies (first-order C.I.),⁶ but it is slowly convergent¹⁷ for other types of correlation effects, as in the helium atom.

As the number of electrons, N , or the number of orbitals, M , taken in the finite C.I. basis set increases, the number of configurations corresponding to the virtual excitations of three, four, . . . electrons at a time increases as N^3 , N^4 , . . . or M^3 , M^4 , . . . Thus, even with a molecule like CH_4 , one rapidly runs into thousands of configurations.

Accurate calculations on two-electron systems, e.g. He and H_2 , have been possible through the use of the interelectronic coordinate r_{12} in the wave function directly.* Such "closed form" methods are discussed in detail by Löwdin.¹

Many attempts^{1,18,19} were made to extend this " r_{12} -coordinate" method to N electrons by multiplying the determinantal wave function by a correlation factor containing all the r_{ij} 's. The main difficulty in these is with the integrals,¹⁹ which contain several r_{ij} 's arising from many-electron terms in the energy.

Besides computational difficulties, these methods treat each atom or molecule as a distinct numerical problem. They do not make use of the separate behavior of shells, bonds, etc., as semi-empirical methods do, nor do they recognize the existence of more than one kind of correlation effect even within the same atom or molecule.

Other attempts were made^{20,21} to separate groups of electrons and to put correlation into each group. The total wave function was taken as the antisymmetrized product of group functions

* For a comparison of the C.I. and r_{12} methods for He see p. 48 of Reference 17.

Λ_A , Λ_B , etc., assumed to satisfy the arbitrary and restrictive orthogonality conditions

$$\langle \Lambda_A(i,j,k, \dots, N_A), \Lambda_B(i,m,n, \dots, N_B) \rangle_{\mathbf{x}_i} = 0 \quad (1)$$

where $\langle \rangle_{\mathbf{x}_i}$ means integration over electron $\mathbf{x}_i$ only. A sigma-pi separation was also based on this approach.²²

The assumed wave function and Eq. (1) are equivalent to assuming the desired result, i.e. the separability of groups, at the outset. Also, correlations between groups, e.g. Van der Waals attractions, are not included; extensions²⁴ to include them do not seem possible (see Section XXVIII). Even for *intra*-shell effects the formalism provides no advantages such as the use of the " r_{12} -method". Its limitations have been discussed elsewhere^{3,23,24,25} (see also Section XXVII).

During recent years, there has been much development in the other many-body problems of physics, e.g. nuclear matter (Brueckner theory) and the electron gas.^{1,26} The possibility of applying these theories to atomic and molecular problems has been considered.¹ It turns out, however, that in atoms and most molecules the many-body problem is physically very different from the other^{9a} problems.

The Brueckner theory is a generalized SCF method^{26,27,48,53} in which orbitals are adjusted to correlation. Why such adjustment is not necessary in the case of atoms and molecules is shown in Sections XV and XIX. Sections XV, XVIII, and XIX compare such theories with the "many-electron theory" of this article.

V. PLAN OF THE MANY-ELECTRON THEORY

The above discussion shows that (i) semi- and non-empirical schemes must be provided with a common basis, and (ii) in the non-empirical theory too, an atom or molecule must be built up piece by piece, but the difficulty of the method must not increase rapidly with the number of electrons, N .

The chemical simplifications which should be introduced have been clear on an intuitive basis for a long time. It is now necessary to introduce the chemical picture in a rigorous and well defined way. In fact, the "picture" truly existing in nature should be

derivable from quantum mechanics and not have to be introduced in an *ad hoc* manner.

To this end, the approach taken below is to start with an exact expression for the wave function ψ and the energy E of a many-electron system. Such an expression is, of course, equivalent to the original Schrödinger equation, but is in such a detailed form that various correlation effects, etc., are explicit in it. From this, major correlation effects are isolated, but a means of estimating everything that is left over is also given. Semi- and non-empirical theories, then, differ only in the means by which their major parts are calculated. This approach also shows the connection between different theories; one looks at what portions of the exact ψ or E give the Brueckner method, say.

The theory will not be based on any infinite series expansion so that where necessary "closed form" methods such as the " r_{12} -coordinate" or "open shell" method,¹ etc., can be used. It should be recognized, however, that there is no particular advantage in generalizing^{1,18,19} the Hylleraas¹ method directly by putting in the r_{ij} 's for all the electron correlations. The many types of correlation effects existing even within the same system necessitate different means of evaluation for each once the separation is achieved.

The overall plan involves:

- (i) The examination of various effects in the exact ψ and E .
- (ii) Methods for obtaining the correlations in shells or electron pairs and between groups.
- (iii) Physical meaning and estimation of remaining errors due to many-electron terms and effects of correlation on orbitals.
- (iv) Based on the general theory, methods for the calculation of properties listed in Section I, also for large atoms and molecules.

To do this we start with MO's even when dealing with a large saturated molecule such as *n*-decane. First, "concentric" or inner and outer shells are separated. When we come to localized groups within the same shell such as C—H or C—C bonds, the lone pairs of H₂O, NH₃, etc., it will not be necessary to start anew with a different *ad hoc* theory for such groups. A simple rigorous transformation localizes the correlation effects and relates them to the general theory which began with the MO description.

Part of the theory below is devoted to the examination of the small residual effects so that the approximations may be checked. Readers interested in practical applications only and who are willing to take the final working form of the theory for granted may proceed directly to Sections XVI, XVII, and XXII on.

VI. ORBITALS

The Hartree-Fock method gives good charge distributions because in finite systems it puts in mainly the long-range part of the Coulomb repulsions between electrons.^{9a} This also makes the remaining correlation effects simple and their theory practicable. Thus the Hartree-Fock method is an excellent starting point.

Hartree-Fock results are rapidly becoming available on atoms and small molecules.²⁸ It is still difficult to obtain Hartree-Fock orbitals for large systems. However, a theory of many-electron systems which takes H.F. as the starting point is useful even for molecules for which accurate H.F. results are not yet available. This is because H.F. also has the formal role of making the rest of the exact ψ and E come out simple. General conclusions, for example semi-empirical ones based on these formal results concerning correlation, are valid even if detailed H.F. orbitals are not known. Further, additional effects coming from the H.F. orbitals being approximated by say LCAO MO's can also be examined on these forms which are given by the theory for the wave function and energy. Correlation effects are not very sensitive to how good the H.F. orbitals are. It should be kept in mind, however, that in just the orbital part of the problem, the use of simple Slater orbitals instead of H.F. usually gives errors comparable to correlation.²⁹

For a closed shell system there is only one Hartree-Fock method. For non-closed shells, however, various H.F. methods are possible. Different orbitals for the same non-closed configuration are obtained depending on which term [e.g. ^3P or ^1D or ^1S in $C(1s^2 2s^2 2p^2)$] is used. Also, different approximations are possible to avoid the off-diagonal energy parameters λ_{ij} , which cannot be transformed away as in the closed shell case. About nine variants of such H.F. methods have been discussed in the literature. To list and discuss

them all would take us too far afield, and the reader is referred to other reviews that deal mainly with H.F.^{17,30,31} Fortunately, these variants often give energies differing from one another by less than 0.01 ev. Note, however, that the “*correlation energy*” of a non-closed shell system depends on which H.F. method is used.

For highest accuracy, different orbitals are obtained for each multiplet.^{28a} The need for simplicity in large systems and also in formulating the theory of correlation dictates however that:

- (i) the same orbitals should be used in all the excited states arising from the same configuration;
- (ii) the H.F. potential V_i acting on an electron i should be the same for all the electrons;
- (iii) orbitals should be orthonormal; and
- (iv) λ_{ij} should be absent from the one-electron equations.

The method³² that satisfies these requirements is a combination of a method discussed by Shortley and Slater¹³ and the “symmetry and equivalence restrictions” method of Nesbet.¹⁶ The *average energy of a configuration*¹³ [e.g. the average energy of $C(1s^2 2s^2 2p^2)$] is varied. In the resulting H.F. equations the V_i ’s are made the same by adding the needed fractions of Coulomb or exchange potentials. These small terms later appear as perturbations in the correlation part of the problem.

A similar starting point has been suggested by Ruedenberg³³ for π -electron systems.

Cases intermediate between closed and non-closed shells also exist. Two types of such “near-degeneracy” are of particular importance:

(a) Consider the isoelectronic series Be, B^+ , C^{2+} , . . . for instance. As the atomic number $Z \rightarrow \infty$, the outer shell $2s^2$ becomes³⁴ degenerate with $2p^2$.

(b) Near-degeneracies arise in diatomic molecules near dissociation.¹ The $(1\sigma_g)^2$ of the H_2 molecule becomes degenerate with the $(1\sigma_u)^2$ configuration as the internuclear distance $r \rightarrow \infty$.

In such intermediate cases it is a matter of convenience how “extended”¹ a Hartree-Fock method is used and how much is left as “correlation”. This problem is discussed further in Sections XIX, XX, and XXI.

VII. ANTISYMMETRY AND RELATIVE ELECTRON DISTRIBUTIONS

The orthogonality of orbitals in closed shells is a consequence of antisymmetry. This forces the electrons into a shell structure ("concentric" shells); but the effect of $\mathcal{A}$, the antisymmetrizer, in localizing electrons goes beyond the rule of "two electrons per orbital".

Hartree-Fock orbitals, or in molecules SCF MO's, individually are suitable for describing electronic excitations and ionization. On the other hand, the shape of a single orbital by itself does not necessarily show the spatial probability distribution of one electron relative to the others.^{35a,35b,35c} Such a distribution is determined by the overall H.F. wave function after the spin-orbitals are multiplied together and antisymmetrized.

For instance, within the neon atom ($1s^2 2s^2 2p^6$) there is no one electron whose distribution looks like $2s$, or like $2p_z$. The $\mathcal{A}$ in the H.F. wave function tends to keep electrons with like spins as far apart from each other as possible. Thus in Ne, one finds two tetrahedra free to rotate relative to one another.^{35a,35b,35c}

In saturated molecules such spin correlation or antisymmetry effects, combined with nuclear geometry, localize electrons into lone pairs and electron pair bonds. Thus an H.F. MO wave function implicitly contains the localization properties.*

The theory below will show that electron correlation (i.e. coulombic correlation, which is the concern of this article, as distinct¹ from the spin or Fermi correlation above which is already in the H.F. wave function) is of a quite localized character in most molecules, particularly saturated ones. This means that the relative electron distributions, and hence the shapes of molecules, are determined mainly by the H.F. part of the w.f.; the correlation part is ineffectual (see also Reference 82). Good H.F. cal-

* These important properties in molecular orbital theory were studied by Lennard-Jones,^{35a} and Pople.^{35b} Linnett^{35c} examined the relative charge distributions by finding the maximum of the square of the determinantal wave functions with respect to variations in the relative positions of all the electrons. In this work, however, bare nuclei, i.e. non-shielded orbitals, were used. Also, it was not recognized that no spin correlation between α and β spins can exist in a closed shell system.

culations³⁶ are becoming available on H_2O , NH_3 , etc.* The above hypothesis would be confirmed if these gave the correct bond angles.^{43,36}

Coulson^{37a} and Lennard-Jones^{35a,37b} have shown that *relative* charge distributions are better represented by a unitary transformation of the H.F. MO determinant which leaves it unchanged but expresses it in terms of localized or "equivalent" orbitals. In a symmetric case, like CH_4 , this transformation³⁷ is unique,[†] but where all the bonds are not equivalent, as in C_2H_6 , a criterion is required. The transformation may be defined, for instance, by requiring the magnitude of the exchange terms to be a minimum. This would give the most localized and the most nearly classical bonds.^{39,46‡}

For large molecules, the Hartree-Fock theory is still in the developmental stage.^{41,42} Simplifications should be possible for large saturated molecules, however. Electrons move not only in the H.F. (MO) potentials of all the electrons, but also in the field of the nuclei. The resulting potential seen by an electron in one end of a molecule say due to the electrons in another bond is therefore a shielded one, i.e. it is of short range.³³ For example, in ethane the average potential of a hydrogen atom on one carbon dies off before reaching a H-atom on the other.⁴³ This suggests that one should obtain the C—H part of the C_2H_6 w.f. from methane, then make the minor adjustments to the SCF between the CH_3 groups and the C—C perhaps by perturbation theory to get the overall SCF.

In the many-electron theory we shall always start with SCF MO's, then transform the H.F. wave function into the localized description where this is required.

* These molecules are considered distortions from the basic tetrahedron. The two separate tetrahedra in a neon-like ion become one as protons are added. This picture is a gross simplification, however, which cannot account for quantitative issues like why the bond angle gets closer to 90° in the series H_2O , H_2S , H_2Se , etc. It recognizes only the exclusion-principle-type hybridization (in Ne), but not the polarization-type hybridization due to the protons. Of course both types are implicit in a complete Hartree-Fock SCF MO calculation.⁴³

† Nesbet³⁸ has obtained approximate SCF MO's with a small gaussian basis set for CH_4 and then transformed them into equivalent orbitals.

‡ The criterion used by Boys⁴⁰ is similar, though conceptually less satisfactory. He separates the centroids of bonds as far as possible.

VIII. HARTREE-FOCK EQUATIONS

Consider an N -electron system with the exact w.f. $\psi(\mathbf{x}_1, \mathbf{x}_2, \dots, \mathbf{x}_N)$ in which each electron i is designated by the space, spin coordinates $\mathbf{x}_i$. In the non-relativistic Schrödinger equation

$$H\psi = E\psi \quad (2)$$

$$H = \sum_{i=1}^N h_i^0 + \sum_{i>j=1}^N g_{ij} \quad (3)$$

$$h_i^0 \equiv -\frac{1}{2}\nabla_i^2 - \sum_{\alpha} \frac{Z_{\alpha}}{R_{\alpha i}} \quad (4a)$$

where h_i^0 is the bare-nuclei Hamiltonian of electron i , $R_{\alpha i}$ is the distance of electron i to nucleus α ,

$$g_{ij} \equiv 1/r_{ij} \quad (4b)$$

and atomic units (1 a.u. = 27.2 eV) are used. The theory will be based on Eqs. (2) and (3); relativistic effects are discussed in Section XXIX.

Consider first the corresponding Hartree-Fock problem for a closed shell system where we have

$$H_0\phi_0 = E_0\phi_0 \quad (5)$$

and

$$\phi_0 = \mathcal{A}(123 \dots N) \quad (6a)$$

$\mathcal{A}$ is the N -electron antisymmetrizer

$$\mathcal{A} = \frac{1}{\sqrt{N!}} \sum_P (-1)^P P \quad (6b)$$

Spin-orbitals are designated by the numerals i starting with the lowest orbital with spin α . Thus in atoms:

$$1 \equiv (1s\alpha), \quad 2 \equiv (1s\beta), \quad 3 \equiv (2s\alpha), \dots \quad (6c)$$

In diatomic molecules

$$1 \equiv (1\sigma_g\alpha), \quad 2 \equiv (1\sigma_g\beta), \quad 3 \equiv (1\sigma_u\alpha), \dots$$

In large molecules, i are still the H.F. SCF MO's. (For the transformation of ϕ_0 and the H.F. equations into equivalent orbitals see

Section XXVII.) Then all odd integers are for α spins, all even ones for β .

In Eq. (6a), before $\mathcal{A}$ is applied, *spin-orbital* i is occupied by electron $\mathbf{x}_i$. Thus

$$\phi_0 = \mathcal{A}\{1(\mathbf{x}_1)2(\mathbf{x}_2) \cdots N(\mathbf{x}_N)\} \equiv \mathcal{A}(1_1 2_2 3_3 \cdots N_N) \quad (6d)$$

so that, in general, when no subscripts are specified as in Eq. (6a), i refers *either to a spin-orbital or to its electron*.

$$H_0 = \sum_{i=1}^N (h_i^0 + V_i) \equiv \sum_{i=1}^N h_i^{\text{eff}} \quad (7)$$

V_i is the H.F. potential of the entire N -electron medium (the H.F. "sea") acting on electron i :

$$V_i(\mathbf{x}_i) = \sum_{j=1}^N \bar{S}_j(i) \quad (8)$$

where $\bar{S}_j(i)$ is the Coulomb (S_j) plus the exchange (R_j'') potential of spin-orbital j acting on i :

$$\bar{S}_j(i) = S_j(i) - R_j''(i) \quad (9a)$$

$$S_j(i) \equiv S_j(\mathbf{x}_i) = \langle j(\mathbf{x}_j), g_{ij} j(\mathbf{x}_j) \rangle_{\mathbf{x}_j} \quad (9b)$$

$$R_j''(\mathbf{x}_i) i(\mathbf{x}_i) = \langle j(\mathbf{x}_j), g_{ij} i(\mathbf{x}_j) \rangle_{\mathbf{x}_j} j(\mathbf{x}_i) \quad (9c)$$

Again $\langle \rangle_{\mathbf{x}_j}$ means integration over coordinates $\mathbf{x}_j$ only. Equation (8) formally includes the $j = i$ terms, namely the "self-potentials".

The sum of V_i in Eq. (7) can be written as a sum of pair potentials

$$\sum_{k=1}^N V_k(\mathbf{x}_k) = \sum_{i>j=1}^N [\bar{S}_i(j) + \bar{S}_j(i)] \equiv \sum_{i>j}^N \bar{S}_{ij}(i, j) \quad (10)$$

In Eq. (7) we have

$$E_0 = \langle \phi_0, H_0 \phi_0 \rangle = \sum_{i=1}^N \varepsilon_i \quad (11)$$

where ε_i is the H.F. orbital energy of i and is approximately equal to the ionization potential¹ from that orbital.

Spin-orbitals satisfy

$$e_i i = 0 \quad (12)$$

where

$$e_i \equiv h_i^0 + V_i - \varepsilon_i$$

Note that the usual total H.F. energy is not E_0 , but

$$E_{\text{H.F.}} = \langle \phi_0, H \phi_0 \rangle = E_0 + E_1 \quad (13a)$$

$$E_1 \equiv \langle \phi_0, H_1 \phi_0 \rangle = - \sum_{i>j}^N (J_{ij} - K_{ij}'') \quad (13b)$$

with

$$H_1 = \sum_{i>j}^N g_{ij} - \sum_{i=1}^N V_i \quad (14)$$

from Eqs. (3) and (7).

J_{ij} and K_{ij}'' are the Coulomb and exchange integrals

$$J_{ij} = \langle ij, g_{ij} ij \rangle; \quad K_{ij}'' = \langle ij, g_{ij} ji \rangle \quad (15a)$$

$$J_{ij} - K_{ij}'' \equiv \bar{J}_{ij} \quad (15b)$$

Combining Eqs. (3), (7), (10) through (15), we define

$$H - E_{\text{H.F.}} = (H_0 - E_0) + (H_1 - E_1) = \sum_{i=1}^N e_i + \sum_{i>j}^N m_{ij} \quad (16)$$

where

$$m_{ij} \equiv g_{ij} - \bar{S}_{ij} + \bar{J}_{ij} \quad (17)$$

m_{ij} represents the "instantaneous" deviation of the potential between electrons i and j from the corresponding average value given by H.F. Thus it may be termed the *fluctuation potential*. Being a residual potential beyond the H.F. one, it is responsible for correlation.

For a non-closed shell system, instead of Eq. (6a) there may be a linear combination of several degenerate determinants ("codetors"). The H.F. equations and V_i will then depend on which of the H.F. methods (Section VI) has been used. The one based on the "average energy of a configuration" with "symmetry and equivalence restrictions" gives the same H_0 and V_i as in Eq. (7) and for all the multiplets arising from that configuration. This also simplifies the treatment of the correlation part.

The Hartree-Fock method applied to the lowest closed and non-closed shell configurations defines an electronic level scheme.

Very often this is in a one-to-one correspondence with the experimentally observed sequence of states.¹⁷ The first two Hund's rules can be understood on the basis of H.F. theory alone. Such level schemes will be referred to as "*adiabatic level schemes*". The H.F. equations above apply to them directly. In rare cases like the $\text{Mg}(3s\ 3d)$ mentioned⁴⁴ in Section II the levels may cross. The correct level scheme will then be given either by the introduction of the correlation as described in Section XXII-B, or by first order C.I.⁶ or by "extending"¹ the H.F. to configurations that mix very strongly (see Sections XIX, XX, and XXI). In the last case the equations of this section would be modified accordingly.

It will be convenient to develop the many-electron theory given below mainly on the basis of closed shells, starting from Eqs. (6)–(17). Minor modifications of the results of forthcoming sections necessary for non-closed shells are indicated in Section XX.

IX. THE EXACT MANY-ELECTRON WAVE FUNCTION

Any exact wave function can be written as

$$\psi = \phi_0 + \chi \quad (18)$$

with a change in normalization. ϕ_0 may be the closed or non-closed shell H.F. w.f. and χ everything that is left over so that

$$\langle \phi_0, \chi \rangle = 0 \quad (19a)$$

$$\langle \phi_0, \phi_0 \rangle = 1; \quad \langle \psi, \psi \rangle = 1 + \langle \chi, \chi \rangle \quad (19b)$$

The H.F. ϕ_0 puts in the repulsions between electrons averaged over their orbitals; χ then brings in all the residual electron–electron repulsion effects. Thus χ is caused by the *fluctuation potentials* $\sum_{i>j}^N m_{ij} = H_1 - E_1$ [Eqs. (14) and (17)]; it is the *exact correlation wave function*.*

For a closed shell system, the *exact* χ is given by^{9,10}

$$\chi = \sum_{i=1}^N \{f_i\} + \sum_{i>j}^N \{\hat{U}'_{ij}\} + \sum_{ijk}^N \{\hat{U}'_{ijk}\} + \dots + \{\hat{U}'_{123\dots N}\} \quad (20a)$$

* Note that in a w.f.¹ like $B(12)[1 + \bar{\alpha}r_{12}]$, e.g. for He, the second term is not the correlation part. It is not orthogonal to $B(12)$ and so it still contains some of the H.F. wave function.

where

$$\{f_i\} \equiv \mathcal{A} \left\{ (123 \dots N) \frac{f_i}{(i)} \right\} \quad (20b)$$

$$\{\hat{U}'_{ij}\} \equiv \frac{\mathcal{A}}{\sqrt{2!}} \left\{ (123 \dots N) \frac{\hat{U}'_{ij}}{(ij)} \right\} \quad (20c)$$

$$\{\hat{U}'_{ijk}\} \equiv \frac{\mathcal{A}}{\sqrt{3!}} \left\{ (123 \dots N) \frac{\hat{U}'_{ijk}}{(ijk)} \right\} \quad (20d)$$

$$\{\hat{U}'_{123\dots N}\} \equiv \frac{\mathcal{A}}{\sqrt{N!}} \left\{ \hat{U}'_{123\dots N} \right\} \quad (20e)$$

The H.F. ϕ_0 may be thought of as a “medium” in which electrons move, each seeing a static potential V_i . Equation (20) then corrects for the “collisions” among progressively larger numbers of electrons at a time in this “medium”. We say that there is a “collision” if, for example, electrons i and j come within the range of their mutual fluctuation potential m_{ij} . Their motions then become *correlated*, with a corresponding correction $\{\hat{U}'_{ij}\}$ in χ . By analogy with imperfect gas theory,⁴⁵ one may speak of one-, two-, three-, etc., electron “clusters” in Eq. (20).

Each $\hat{U}'$ is antisymmetric under an odd number of permutations, i.e.

$$\hat{U}'_{ij}(\mathbf{x}_i, \mathbf{x}_j) \equiv \hat{U}'_{ij}(i, j) = -\hat{U}'_{ij}(j, i) \quad (21)$$

$$\hat{U}'_{ijk}(i, j, k) = -\hat{U}'_{ijk}(j, i, k) \quad \text{etc.}$$

This is why the $(n!)^{-\frac{1}{2}}$ factors appear in Eqs. (20c) to (20e). The permutation group of n -electrons is a subgroup of the N -electron permutation group. We have

$$\begin{aligned} \mathcal{A}^2 &= (N!)^{\frac{1}{2}} \mathcal{A} \\ \mathcal{B}_{ij\dots n}^2 &= (n!)^{\frac{1}{2}} \mathcal{B}_{ij\dots n} \end{aligned} \quad (22)$$

also

$$\begin{aligned} \mathcal{A} \mathcal{B}_{ij} &= (2!)^{\frac{1}{2}} \mathcal{A} \\ \mathcal{A} \mathcal{B}_{ijk} &= (3!)^{\frac{1}{2}} \mathcal{A} \end{aligned} \quad (23)$$

and similarly for all $\mathcal{B}_{ij\dots n}$ where $\mathcal{B}_{ij\dots n}$ is an n -electron antisymmetrizer.

Each function is *orthogonal to all the spin-orbitals occupied in ϕ_0* , i.e.

$$\left. \begin{aligned} \langle \hat{f}_i, k \rangle &= 0 \\ \langle \hat{U}'_{ij}, k \rangle &= 0 \\ \dots \\ \langle \hat{U}'_{ijk\dots N}, k \rangle &= 0 \end{aligned} \right\} \quad (k = 1, 2, \dots, i, \dots, j, \dots, N) \quad (24)$$

where, e.g.,

$$\begin{aligned} \langle \hat{U}'_{ij}, k \rangle &\equiv \langle \hat{U}'_{ij}(\mathbf{x}_i, \mathbf{x}_j), k(\mathbf{x}_i) \rangle_{\mathbf{x}_i} \\ &= \int \hat{U}'_{ij}^*(\mathbf{x}_i, \mathbf{x}_j) k(\mathbf{x}_i) d\mathbf{x}_i \end{aligned} \quad (25)$$

This “orbital orthogonality” is designated by the caret ($\hat{}$). The (*) designates complex conjugate.

Note that both Eqs. (20) and (24) are rigorous.^{8,9} The latter are *not* assumed restrictions as Eq. (1) was.

Though Eq. (20) is still formal, it has distinct advantages over say the infinite exact C.I. series: (i) it is *not* an infinite series if the system has a finite number (N) of electrons; (ii) it is in a very detailed form so that each term can be examined and systematic approximations can be applied, as we do below; and (iii) the $\hat{U}'$ functions are in a closed form. They may contain interelectronic coordinates, “split shells”, etc., or each may be separately expanded in a C.I. series.

Equations (20) and (24) can be obtained⁸ by solving each order of the wave function in the perturbation theory using operator techniques to give the closed forms $\hat{U}'_{ij}$, $\hat{U}'_{ijk}$, etc. In the first-order χ_1 for instance,⁸ starting with ϕ_0 as unperturbed, one finds only the $\hat{u}_{ij}^{(1)}$ (first order). In χ_2 , the second-order parts of $\hat{u}_{ij}$, i.e. $\hat{u}_{ij}^{(2)}$, appear as well as $\hat{f}_i^{(2)}$ and $\hat{U}_{ijk}^{(2)}$. More and more terms appear in the higher orders. One then lumps together, say, all the pair terms $\hat{u}_{ij}^{(1)}$, $\hat{u}_{ij}^{(2)}$, . . . from all orders and calls the sum $\hat{U}_{ij}$, and similarly for $\hat{U}_{ijk}$ and so on.

Alternatively, the exact χ can be obtained from its infinite C.I. series form. This expansion¹ contains all the unique “ordered”¹ Slater determinants formed from a complete one-electron basis set. If ϕ_0 is to be H.F., the basis set must start with the N H.F. spin-orbitals, but the rest of it is arbitrary.¹ The C.I. may be

classified³ into single, double, etc., "excitations" from particular spin-orbitals in ϕ_0 . If now each class is summed^{3,9a,25} making use of the completeness of the basis set, Eqs. (20) and (24) result. The arbitrariness of the basis set, except for its first N H.F. orbitals, is equivalent to $\hat{U}'$ being as yet an undetermined closed function but subject to Eqs. (24). However, below, we shall put Eq. (20) into a still more detailed form and bring out effects not seen in C.I.

The χ of Eq. (20) can be derived in still another, but most powerful way which also shows how the different parts of χ (e.g. the f_i 's or $\hat{U}_{ij}$'s, etc.) can be obtained from any ψ . This may be called "the method of *successive partial orthogonalizations*".

Take the exact many-electron w.f. ψ and Schmidt orthogonalize it to ϕ_0 ; by definition [see Eq. (19a)] the result is χ :

$$\chi = \psi - \langle \psi, \phi_0 \rangle \phi_0 = \psi - \phi_0 \quad (26)$$

$\langle \psi, \phi_0 \rangle = 1$ because of Eqs. (19) and (26), by choice. Next orthogonalize χ to spin-orbital products obtained from ϕ_0 by dropping one of the spin-orbitals each time, e.g. to $(23 \dots N)$, $(134 \dots N)$, etc. The result χ' is a smaller portion of χ :

$$\chi' = \chi - \sum_{i=1}^N \det \left\{ \left\langle \chi, \frac{(123 \dots N)}{(i)} \right\rangle \left\langle \frac{(123 \dots N)}{(i)} \right\rangle \right\} \quad (27)$$

"det" is $\sqrt{N!} \mathcal{A}$ and $\langle \chi, (123 \dots N)/(i) \rangle$ means integration over all coordinates except $\mathbf{x}_i$, the one corresponding to the spin-orbital i which is missing from the orbital product. There is no antisymmetrizer in this integral, because χ itself is antisymmetric [see Eqs. (23)].

Each integral in Eq. (27) gives a function of $\mathbf{x}_i$ only and defines

$$f_i \equiv \sqrt{N!} \langle \chi, [123 \dots (i-1)(i+1) \dots N] \rangle \quad (28)$$

Thus, so far we get

$$\psi = \phi_0 + \sum_{i=1}^N \mathcal{A} \left\{ (123 \dots N) \frac{f_i}{i} \right\} + \chi' \quad (29)$$

and

$$\langle f_{i,k} \rangle = 0 \quad (k = 1, 2, 3, \dots, i, \dots, N) \quad (30)$$

To see how Eq. (30) comes about, consider the four-electron case for simplicity of notation. Using the definition of $\hat{f}_i$, Eq. (28),

$$\langle \hat{f}_1, 1 \rangle = \sqrt{4!} \langle \chi, 1_1 2_2 3_3 4_4 \rangle = \langle \chi, \phi_0 \rangle = 0 \quad (31a)$$

$$\langle \hat{f}_1(\mathbf{x}_1), 2(\mathbf{x}_1) \rangle = \sqrt{4!} \langle \chi, 2_1 2_2 3_3 4_4 \rangle = \langle \chi, \mathcal{A}(2_1 2_2 3_3 4_4) \rangle = 0 \quad (31b)$$

and so on with $k = 3, 4$. In the last parts of Eqs. (31a,b) we have used Eq. (22) and the fact that $\mathcal{A}$ is Hermitian.

Note that "orthogonalizations" as in Eq. (27) differ from the usual kind, such as those of Eq. (26); an N -electron function is being orthogonalized to a function of fewer electrons.⁸ This is why the "det"'s appear in Eq. (27).

Equation (29) is continued by the Schmidt "orthogonalization" of the remainders χ' , χ'' , . . . to the products of fewer and fewer spin-orbitals out of ϕ_0 . Thus

$$\chi'' = \chi' - \sum_{i>j}^N \det \left\{ \left\langle \chi', \frac{(123 \dots N)}{(ij)} \right\rangle \left\langle \frac{(123 \dots N)}{(ij)} \right\} \right\} \quad (32)$$

Again, as in Eqs. (28) to (31),

$$\hat{U}'_{ij} \equiv \langle \chi', [123 \dots (i-1)(i+1) \dots (j-1)(j+1) \dots N] \rangle \quad (33)$$

$$\langle \hat{U}'_{ij}, k \rangle = 0 \quad (k = 1, 2, \dots, i, \dots, j, \dots, N) \quad (34)$$

and in the notation of Eq. (20)

$$\psi = \phi_0 + \sum_{i=1}^N \{ \hat{f}_i \} + \sum_{i>j}^N \{ \hat{U}'_{ij} \} + \chi'' \quad (35)$$

In this way the entire Eqs. (20), (21), and (24) are derived, with the additional result that the general term is given by

$$\hat{U}'_{\underbrace{ijk\dots n}_q} = \sqrt{\frac{N!}{q!}} \left\langle \chi^{(q-1)}, \underbrace{\frac{(123 \dots N)}{(ijk \dots n)}}_q \right\rangle \quad (36)$$

Brenig⁴⁷ has applied a somewhat related procedure to the Schrödinger equation $H\psi = E\psi$. Multiplying both sides by products of $(N-1)$, $(N-2)$, . . . , 1 spin-orbitals at a time and integrating he gets a set of coupled integro-differential equations analogous to the Kirkwood-Bogoliubov equations in the theory of fluids.⁴⁵ The equation for $\hat{f}_i$ depends on $\hat{U}'_{ij}$, $\hat{U}'_{ijk}$, . . . , the

one for $\hat{U}'_{ij}$ on f_i , $\hat{U}'_{ijk}$, etc. These do not have any practical utility, however. Even if they were decoupled by approximations (e.g. similar to the "superposition approximation"⁴⁵ of Kirkwood for liquids)⁴⁷ that would lead to errors difficult to assess, they still could not be solved directly.

Equations (35) and (36) on the other hand are capable of giving specific results, especially when used along with the variation principle

$$E \leq \langle \tilde{\psi}, H \tilde{\psi} \rangle / \langle \tilde{\psi}, \tilde{\psi} \rangle \quad (37)$$

For, suppose one had a good trial function $\tilde{\psi}$. Then from Eqs. (36) one could obtain its f_i , $\hat{U}'_{ij}$, $\hat{U}'_{ijk}$, etc., components just by integrations.

Many computational schemes and trial functions exist in the literature which by-pass Hartree-Fock and do not show any of the correlation effects explicitly. The LiH, Li₂, etc. calculations of Harris and Taylor⁷¹ and the method of "alternant orbitals"⁷² are examples. Much insight could be gained into these problems by a "successive partial orthogonalizations" analysis.* Suppose such an analysis gave an appreciable f_i or $\hat{U}'_{ijk}$, even though such terms were expected to be small in the exact χ on the basis of considerations such as the ones of Sections XVIII, XIX, then a better trial function as judged by the energy would be obtained by removing them. We shall actually carry out such analyses for He with r_{12} in $\tilde{\psi}$ and for many-electron systems to examine the importance of f_i (Section XIX).

X. ORBITAL ORTHOGONALITY

Equations (24) actually imply two different effects.^{8†} Each $\hat{U}'_{ijn}$ is orthogonal (a) to its own orbitals $i, j, l, \dots$, and (b) to all the others $k \neq i, j, l, \dots$, occupied in ϕ_0 .

Effect (a) comes about because correlations involving fewer

* It has now been shown that this method also gives a way of obtaining the Hartree-Fock w.f. directly from a general many-electron trial function without a separate variational calculation. See "Notes added in proof" at the end of this article.

† See also References 48a and 48b. These authors only used the exclusion effect, i.e. (b).

electrons than in the $\hat{U}$ under consideration have been separated out as in Eqs. (32) and (35). This is of particular importance in $\hat{U}'_{ij}$, where the $\hat{f}_i$ are separated out. The $\hat{f}_i$, the one-electron terms, represent the effect of correlation on orbitals (Section XIX).

To clarify this point let us look at the helium atom in some detail. Then

$$\phi_0 = \mathcal{B}(12) \quad (38)$$

is the $1s^2$ H.F. determinant. With $\psi(\mathbf{x}_1, \mathbf{x}_2)$ the exact $1S$ w.f.

$$\psi(\mathbf{x}_1, \mathbf{x}_2) = \mathcal{B}(12) + u_{12}^o \quad (39)$$

where $\chi_{He} \equiv u_{12}^o(\mathbf{x}_1, \mathbf{x}_2)$ as in Eq. (18). Applying Eqs. (27) to (29)

$$\psi = \mathcal{B}(12) + \mathcal{B}\{\hat{f}_1 2\} + \mathcal{B}\{1 \hat{f}_2\} + \hat{U}'_{12} \quad (40)$$

e.g.

$$f_1(\mathbf{x}_1) = \sqrt{2} \langle u_{12}^o(\mathbf{x}_1, \mathbf{x}_2), 2(\mathbf{x}_2) \rangle_{\mathbf{x}_2}, \quad (41)$$

and

$$\langle \hat{U}'_{12}, 1 \rangle = \langle \hat{U}'_{12}, 2 \rangle = 0 \quad (42)$$

In C.I. language, the $\hat{f}_i$'s are the sums of single excitations, and $\hat{U}'_{12}$ of only double excitations.^{3,8} With a complete basis set $\{k\}$, the C.I. series is^{1,3}

$$\psi = \mathcal{B}(12) + \sum_{k>2} c_k \mathcal{B}(1_1 k_2) + \sum_{l>2} c_l \mathcal{B}(l_1 2_2) + \sum_{k>l>2} c_{kl} \mathcal{B}(l_1 k_2) \quad (43)$$

Multiplying this equation by $1(\mathbf{x}_1)$ and integrating, one gets

$$\sqrt{2} \langle \psi, 1 \rangle_{\mathbf{x}_1} = 2(\mathbf{x}_2) + \sum_{k>2} c_k k_2 \quad (44)$$

$$\therefore \sqrt{2} \langle u_{12}^o, 1 \rangle_{\mathbf{x}_1} = \hat{f}_2(\mathbf{x}_2) = \sum_{k>2} c_k k_2 \quad (45)$$

and

$$\hat{U}'_{12} = \sum_{k>l} c_{kl} \mathcal{B}(kl) \quad (46)$$

This is how Eqs. (20) and (24) could also be proved using C.I.

With this example we see that effect (b) above cannot occur in

the helium atom, but only in a many-electron system. We have, for example,

$$\langle \hat{U}'_{ij}, k \rangle = 0 \quad \begin{matrix} k \neq i, j \\ (1 \leq k \leq N) \end{matrix} \quad (47)$$

which means that when electrons i and j are correlating, i.e. "colliding" with one another, they are prevented by the Pauli Exclusion Principle from going into the spin-orbitals ($k \neq i, j$) of ϕ_0 already occupied; hence the name "exclusion effect".^{3,8} In C.I. with more than two electrons, this means that the last sum of Eq. (43) begins above N

$$\sum_{k > l > N}^{\infty} c_{kl} \mathcal{B}(l_1 k_2) \quad (48)$$

XI. UNLINKED CLUSTERS

The exact χ of Eq. (20) is still not in a detailed enough form. The successive terms in it correct for the effects of progressively larger numbers of electrons interacting with their fluctuation potentials. As in the imperfect gas theory,⁴⁵ however, one must distinguish between two types of "clusters". For example, four electrons may "collide" all at once (a four-body collision) and contribute to $\hat{U}'_{1234}$. But, there may also be two independent binary "collisions" taking place in different parts of an atom or molecule at the same time. We can talk about "time" since the theory could have been based equally well on a time-dependent formalism such as the one used by Goldstone.⁴⁹ Individual binary collisions are already corrected for by the $\{\hat{U}'_{ij}\}$ terms. The simultaneous ones are as yet implicit in the larger clusters. Two independent $\hat{U}'_{ij}$'s together, for example, may correspond to say $\hat{U}'_{12}\hat{U}'_{34}$ and be a part of $\hat{U}'_{1234}$.

The actual many-electron "collisions" are "linked clusters", which we shall denote by $\hat{U}_{ijk\dots}$ *without primes*; products of independent but simultaneous "collisions", e.g. $\hat{U}_{12}\hat{U}_{34}$ or $\hat{U}_{12}\hat{U}_{34}\hat{U}_{56}$, etc., are "unlinked clusters".

Thus each *exact* $\hat{U}'$ in Eq. (20) actually consists of all possible antisymmetrized products of the preceding fewer-electron terms not containing any indices in common, and a new "linked cluster" term $\hat{U}$. For convenience the terms can be designated by diagrams

in which the $\hat{f}_i$'s are represented by small circles (only those to which no lines are attached) and the linked cluster $\hat{U}$'s by straight lines drawn between the linked electrons. For example

$$\hat{U}'_{ij} = \mathcal{B}(\hat{f}_i \hat{f}_j) + \hat{U}_{ij}$$

(49)

$$\hat{U}'_{ijk} = \mathcal{B} \left\{ \hat{f}_i \hat{f}_j \hat{f}_k + \hat{f}_i \frac{\hat{U}_{jk}}{\sqrt{2}!} + \frac{\hat{U}_{ik}}{\sqrt{2}!} \hat{f}_j + \frac{\hat{U}_{ij}}{\sqrt{2}!} \hat{f}_k \right\} + \hat{U}_{ijk} \quad (50)$$


(51)

Similarly $\hat{U}_{ijkl}$ consists of the following diagrams


(52)

Here each figure denotes all the terms differing only in the labeling of the electrons.

Coefficients such as the $\sqrt{2}!$ in Eq. (50) come from Eqs. (21) and (23). We have, for example, in Eq. (52)

$$\mathcal{B}_{ijkl} \left\{ \frac{\hat{U}_{ij}}{\sqrt{2}!} \frac{\hat{U}_{kl}}{\sqrt{2}!} + \frac{\hat{f}_i}{\sqrt{1}!} \frac{\hat{U}_{jkl}}{\sqrt{3}!} + \dots \right\} \quad (53)$$

But each $\hat{U}'$ eventually gets antisymmetrized by $\mathcal{A}$, so that using Eqs. (20b-e), $\{\hat{U}'_{ijkl}\}$ contains

$$\begin{aligned} & \frac{\mathcal{A}}{\sqrt{4}!} \left\{ \frac{(123 \dots N)}{(ijkl)} \mathcal{B}_{ijkl} \left(\frac{\hat{U}_{ij} \hat{U}_{kl}}{\sqrt{2}! \sqrt{2}!} + \frac{\hat{f}_i \hat{U}_{jkl}}{\sqrt{1}! \sqrt{3}!} \right) \right\} \\ &= \mathcal{A} \left\{ \frac{(123 \dots N)}{(ijkl)} \frac{\hat{U}_{ij} \hat{U}_{kl}}{\sqrt{2}! \sqrt{2}!} + \frac{\hat{f}_i \hat{U}_{jkl}}{\sqrt{1}! \sqrt{3}!} \right\} \end{aligned} \quad (54)$$

Hence with the notation of Eq. (20)

$$\begin{aligned} \{\hat{U}'_{ijkl}\} &= \left\{ \sqrt{4!} \hat{f}_i \hat{f}_j \hat{f}_k \hat{f}_l + \left(\frac{4!}{1!3!} \right)^{\frac{1}{2}} \hat{f}_i \hat{U}_{jkl} + \dots \right. \\ &\quad \left. + \left(\frac{4!}{2!2!} \right)^{\frac{1}{2}} \hat{U}_{ij} \hat{U}_{kl} + \dots + \left(\frac{4!}{4!} \right)^{\frac{1}{2}} \hat{U}_{ijkl} \right\} \end{aligned} \quad (55)$$

The coefficient of an $(r \times s \times t \times \dots)$ -unlinked cluster which is part of an n -cluster ($n = r + s + t + \dots$) is

$$\left(\frac{n!}{r!s!t!\dots} \right)^{\frac{1}{2}} \quad (56)$$

Note that *the more detailed* χ obtained by the substitution of equations similar to (49)–(52) in Eq. (20) *is still exact*.

As we shall see below, the main mathematical function of “unlinked clusters” is to cancel the normalization terms in the denominator of Eq. (37.) This “cancellation of unlinked clusters”^{49,50} plays an important role in infinite many-body problems,^{26,49} because $\langle \chi, \chi \rangle \rightarrow \infty$ as $N \rightarrow \infty$. The cancellation is automatic in the Rayleigh–Schrödinger (R.S.) perturbation theory⁵⁰ but it must be recognized in variational methods by augmenting the trial functions with unlinked clusters.^{51,9a}

One can see in a very simple way how *some* of the unlinked clusters come in. Take the $\hat{f}_i$ terms for example. These are corrections to the H.F. orbitals i , so suppose that each i in ϕ_0 is replaced by $(i + \hat{f}_i)$ and the products are expanded. Then

$$(i + \hat{f}_i)(j + \hat{f}_j) = (ij) + (i\hat{f}_j) + (\hat{f}_ij) + (\hat{f}_i\hat{f}_j) \quad (57)$$

shows how Eq. (49) comes about [compare Eq. (40)].

The new orbitals are not normalized to unity; therefore $\langle \psi, \psi \rangle$ will contain the term $(1 + \langle \hat{f}_i\hat{f}_i \rangle)$. But the $(\hat{f}_i\hat{f}_i)$ in the w.f. give similar factors in $\langle \psi, H\psi \rangle$. *In general, the closer a trial function approaches the exact χ the more of the denominator $(1 + \langle \chi, \chi \rangle)$ is cancelled* [see the exact energy equation (59) below]. It follows that a trial function can always be improved by the inclusion of unlinked clusters.^{9a}

A “generalized product of group functions”^{20–24} type of $\tilde{\psi}$ [Eq. (1)] puts in *only some of the unlinked clusters*. To see this write the group functions $\Lambda_K(i, j, \dots, n)$ in the form $\mathcal{B}(ij \dots n) + \Lambda^o(i, j, \dots, n)$ such that $\langle \mathcal{B}(ij \dots n), \Lambda^o \rangle = 0$. Then the products $\mathcal{A}(\Lambda_K^o \Lambda_L^o \dots)$ are the only unlinked clusters; the others that are needed are missing.

XII. VARIATION PRINCIPLE AND THE EXACT ENERGY

Assuming the Hartree–Fock ϕ_0 is known, the χ part of ψ must be determined. Substituting $\tilde{\psi} = \phi_0 + \tilde{\chi}$ where $\langle \phi_0, \tilde{\chi} \rangle = 0$ in

Eq. (37) and clearing the denominator of $E_{\text{H.F.}}$, one obtains the variation principle⁵² for χ :

$$E \leq E_{\text{H.F.}} + \frac{2\langle\phi_0, (H - E_{\text{H.F.}})\tilde{\chi}\rangle + \langle\tilde{\chi}, (H - E_{\text{H.F.}})\tilde{\chi}\rangle}{1 + 2\langle\phi_0, \chi\rangle + \langle\tilde{\chi}, \tilde{\chi}\rangle} \equiv \tilde{E} \quad (58)$$

If the exact χ is substituted for $\tilde{\chi}$ and the Schrödinger equation (for χ),⁵² and Eqs. (5), (16), and (19) are used, the denominator is cancelled and Eq. (58) reduces to

$$E = E_{\text{H.F.}} + \langle\phi_0, H_1\chi\rangle \quad (\text{exact } \chi \text{ only}) \quad (59)$$

For a closed shell system and when ϕ_0 is the H.F. w.f., Eq. (59) gives upon substitution of Eqs. (20) and (14)

$$E = E_{\text{H.F.}} + \sum_{i>j}^N \langle\mathcal{B}(ij), g_{ij}\hat{U}'_{ij}\rangle \quad (60)$$

(exact $\hat{U}'_{ij}$ of χ and exact E only)

This is the closed form of the “generalized Brillouin theorem”¹ usually given in C.I. form.^{1,26,31,51} *It holds only for the exact $\hat{U}'_{ij}$ of Eq. (20) and with H.F. orbitals.* Note that the m_{ij} ’s have been reduced to $g_{ij} = 1/r_{ij}$ ’s.

The simplicity of Eq. (60) is only formal. With any trial $\tilde{\chi}$ —as substitution into Eq. (58) will show—this form is lost. Equation (60) cannot be made the basis of semi-empirical arguments like the separation of shells, because the pair terms are not decoupled. The $\hat{U}'_{ij}$ ’s may very well depend on each other strongly and on $\hat{f}_i$, $\hat{U}'_{ijk}$, etc. (In fact, formally they do, through the set of coupled integro-differential equations mentioned above.^{47,53})

A more detailed expression for the energy must be obtained in a variational form by substituting Eq. (20) in Eq. (58). Various correlation energy effects then appear explicitly and can be examined separately. This is, of course, necessary for actual calculations too.

XIII. VARIOUS CORRELATION EFFECTS IN THE EXACT WAVE FUNCTION AND THE ENERGY

The exact χ above, Eqs. (20), (24), (49)–(52), etc., contains (i) the effect of correlation on orbitals, i.e. the $\hat{f}_i$ ’s; (ii)

two-electron correlations, the $\hat{U}_{ij}$ terms of Eq. (49); (iii) many-electron correlations (i.e. $N \geq n > 2$) $\hat{U}_{ijk}$, $\hat{U}_{ijkl}$, . . .; and (iv) the unlinked clusters of all these terms.

Though each of these correlations involves only a few electrons at a time, it is influenced by all the rest of the electrons because the "collisions" take place not in vacuum, but in a "medium"—the Hartree-Fock "sea", ϕ_0 .^{3,8,9} This "sea" affects a "cluster" through

(a) the "exclusion effect", Eq. (47), or in general

$$\langle \hat{U}_{ijl\dots n}, k \rangle = 0 \text{ for } \begin{cases} k \neq i, j, l, \dots, n \\ k \text{ in } \phi_0 \end{cases} \quad (47')$$

and (b) the entire H.F. potential V_i , Eq. (8).

Similar correlation effects arise in the energy. These can be obtained explicitly by substituting χ , Eq. (20), into Eq. (58). The complicated algebra is conveniently carried out with diagrams, as in Eq. (52). The energy matrix element diagrams contain in addition to the solid lines for the $\hat{U}$'s, dotted lines that denote the fluctuation potentials, m_{ij} , Eq. (17). Thus, for example

$$i \text{---} \text{---} j \equiv \langle \mathcal{B}(ij), m_{ij} \hat{u}_{ij'} \rangle \quad (61)$$

Brout⁵¹ has used a similar diagram technique but with a C.I. formalism and in connection with the Brueckner theory for infinite nuclei. The technique used here has little to do with the usual field-theoretic methods⁴⁹ or statistical mechanics.⁴⁵

We shall not write down all the diagrams that come up in the exact energy. Suffice it to say that *a given correlation effect in χ gives rise to additional effects in the energy*. For instance, the energy of a $\tilde{\chi}$ with only $\hat{U}_{ij}$'s in it contains three-electron as well as pair correlations.^{9a} This is related to the fact that the energy is stationary and can be determined to a higher accuracy than and by a given $\tilde{\chi}$.

The complete exact χ and E are equivalent to the Schrödinger equation itself, and so do not provide a workable theory, only a formal one. The significance and accuracy of various approximate theories can be assessed, however, if they are compared with these complete formal expressions. In Section XV, we shall show what portions of the χ and E are involved in which theory.

Many formalisms and theories are possible depending on whether the $\hat{f}_i$'s and $\hat{U}_{ij}$'s or the $\hat{U}'_{ijk}$'s are retained, and so on. Many of these would introduce unnecessary complications, however, by including terms that were physically insignificant in the first place. To arrive at the simplest realistic theory, therefore, the following effects must be examined and their magnitudes estimated for representative cases: (i) pair correlations, $\hat{U}_{ij}$, which are the major effects, (ii) n -electron correlations ($n > 2$), $\hat{U}_{ijk}$, etc., in χ , (iii) n -electron correlations ($n > 2$) that arise in the energy just from the $\hat{U}_{ij}$'s (these will be more significant than the many-electron correlations in χ since the ones in χ give higher "order" effects in the energy involving more electrons); and (iv) $\hat{f}_i$.

These effects are examined in Sections XVIII, XIX, and XX after we have listed which ones are involved in various theories. These theories can be derived from the exact χ and E by a general variation-perturbation approach. This approach, which also allows one to estimate the errors left after a certain approximation has been made, is described first.

XIV. VARIATION-PERTURBATION APPROACH

The straightforward use of the variation method, Eq. (37) or Eq. (58), involves guessing a trial function. One would prefer instead to *derive* a realistic $\tilde{\chi}$ systematically.

The condition that $\tilde{E}(\tilde{\chi})$ [Eq. (58)] be stationary or a minimum is also the condition for the corresponding Euler equation to have a solution. For Eq. (58), the Euler equation is the Schrödinger equation itself, rewritten for χ :

$$\begin{aligned} (H_0 - E_0)\chi &= (\Delta E - H_1)(\phi_0 + \chi) \\ \Delta E &\equiv E - E_0 \end{aligned} \tag{62}$$

which we cannot solve. On the other hand, there may be a large *portion* of $\tilde{E}$, Eq. (58), which when made stationary leads to a Euler equation that can be solved, at least partly.

The variation-perturbation approach then briefly consists of (a) minimizing a large portion (which has a stationary or minimum point) of $\tilde{E}$, Eq. (58), to obtain a trial function $\tilde{\chi}$, and (b) substituting this back into the *entire* E to get an upper limit to E .

The original portion gives the main energy effect, and the rest of E an estimate of the error.

As an example, the entire Rayleigh–Schrödinger (R.S.) perturbation series can be derived this way;⁵² so can the generalized SCF methods and other many-body theories^{9b,10,26} (see Section XV).

Let us take the R.S. case further for future reference.

A large stationary portion of $\tilde{E}$ [Eq. (58) together with Eq. (16)] is

$$\delta\{2\langle\phi_0, (H_1 - E_1)\tilde{\chi}\rangle + \langle\tilde{\chi}, (H_0 - E_0)\tilde{\chi}\rangle\} = 0 \quad (63)$$

This leads to

$$(H_0 - E_0)\chi_1 = (E_1 - H_1)\phi_0 \quad (64)$$

the first-order equation of R.S. theory, and to an upper limit^{54,55}

$$E \leq \frac{E_0 + E_1 + E_2 + E_3}{1 + \langle\chi_1, \chi_1\rangle} \quad (65)$$

where

$$E_2 = \langle\phi_0, H_1\chi_1\rangle; \quad E_3 = \langle\chi_1, (H_1 - E_1)\chi_1\rangle$$

The process is continued further by letting

$$\chi = \chi_1 + \Delta_1 \quad (66)$$

in Eq. (58), clearing the denominator of terms involving only ϕ_0 and χ_1 and obtaining a new remainder in terms of Δ_1 . A large portion of the new remainder is stationary with respect to Δ_1 and gives the second-order R.S. equation (for χ_2) and E_4 and E_5 . The entire R.S. series can be generated in this way.⁵²

We may add that the well known difficulties of using the variation method with *excited states* (m) are circumvented if $\chi_1^m \approx \chi^m$, i.e. if the first-order w.f. for excited state m is a sufficient approximation to the exact w.f. of that state. Then one still has a *minimum* principle⁵⁶ involving only the known, “unperturbed” w.f.’s, ϕ_0^k , of states lower than (m).

The *first approximation* to the many-electron theory of atoms and molecules was derived by solving⁸ Eq. (64) with the H.F. ϕ_0 using operator techniques. The development of Brueckner’s theory of nuclear matter^{50,26} and other many-body theories²⁶ also made much use of perturbation formalism.

The *complete form* of the "Many-Electron Theory", which is the main topic of this article, however, is *not* a perturbation theory. Both the many-electron theory and Brueckner-type theories are now derived from the exact χ and E by the *general* "variation-perturbation" approach. The approach which we call "variation-perturbation" for lack of a better name should not be confused with perturbation theory.

XV. VARIOUS MANY-PARTICLE THEORIES

In the light of the general approach described above, we can see how various many-body theories are related to the exact χ and E . (We shall not discuss here the conventional non-empirical schemes mentioned in Section IV.)

A. Generalized SCF Methods

(a) If only the $\{f_i\}$ terms and a *single* $\hat{U}_{ij}$ (e.g. the π -electron pair in C_2H_4) are kept in χ [Eq. (20)] and Eq. (58) is minimized, one gets coupled integro-differential equations relating the f_i to the $\hat{u}_{ij}$. These may in principle be solved by iterations until the f_i and $\hat{u}_{ij}$ become self-consistent.^{48a} This is essentially the Brueckner method for a single pair only.

(b) The Brueckner method is obtained^{26,51,47} if *all* the $\{f_i\}$'s, $\{\hat{U}_{ij}\}$'s and their unlinked clusters⁵¹ are kept as $\phi_0 + \tilde{\chi}$. In the energy, Eq. (58), this $\tilde{\chi}$ gives matrix elements involving more than one kind of $\hat{U}_{ij}$ (e.g. $\hat{U}_{ij}$, $\hat{U}_{ik}$, etc.) as well as terms with a single $\hat{U}_{ij}$ [see Eqs. (82) and (159) below]. If only the latter are varied along with the f_i terms, the coupled equations which make the f_i 's and $\hat{U}_{ij}$'s self-consistent again result.

Originally, the Brueckner theory was derived in a very different way²⁶ for infinite nuclear matter where the orbitals are plane waves. The Hartree-Fock method cannot be taken as a starting point for nuclear matter, because there the matrix elements over the *hard-core* nucleon-nucleon repulsions are infinite. These interactions are so strong that it cannot be simply assumed that particles move independently in an undisturbed "sea". Brueckner's theory essentially cancelled these infinities by including a "correlation potential" in the potential of the "sea". This was

done, however, in a rather roundabout way using an infinite basis set (as in C.I.) and a complicated double SCF procedure. The method could be used for infinite systems where, for example, the orbitals are already known (still plane waves) and where C.I. summations can be replaced by integrations in momentum space, but for finite systems, e.g. finite nuclei, the theory turned out to be impracticable.⁵⁸⁻⁶⁰

The derivation from χ given here does not involve infinite sums. The $\hat{f}_i$ and $\hat{u}_{ij}$ being in a closed form eliminates at least some of the difficulties and should be useful for finite nuclei^{9b} where the hard-core problem is still crucial. A very elegant Brueckner-type or "reaction operator" theory for finite systems has also been derived by Primas⁵⁷ using Lie-algebra.

The $\hat{f}_i$, i.e. the effects of correlation on orbitals, are indeed very strong in nuclei; they cancel the infinities of the H.F. method by excluding nucleons from each other's hard core.

The double SCF equations are simplified by letting

$$i' = \frac{1}{\sqrt{(1 + \langle \hat{f}_i, \hat{f}_i \rangle)}} (i + \hat{f}_i) \quad (67)$$

be the new orbitals (*Brueckner orbitals*) and replacing the "bare" interactions g_{ij} by the "correlation potentials" (or "reaction matrix" in C.I. language), t_{ij}

$$t_{ij}\mathcal{B}(ij) \equiv g_{ij}[\mathcal{B}(ij) + \hat{U}_{ij}] \quad (68)$$

The SCF equations then become *formally* similar to the H.F. ones.⁵⁹ Note, however, that the greatest difficulty lies in the strong dependence of the t_{ij} and hence of $(V_{i'})_{\text{Brueckner}}$ on the particles they act on,^{9,53} because the $\hat{U}_{ij}$ in Eq. (68) differ greatly from pair to pair.

There have been attempts to apply the Brueckner method to atoms and molecules,^{1,27} but in atoms and molecules where the $g_{ij} = 1/r_{ij}$ are well behaved and H.F. is a perfectly valid starting point, there is no need to use such a method, with all its attendant difficulties,^{9,53} just to include $\hat{f}_i$. It will be shown in Section XIX that the $\hat{f}_i$'s in atoms and molecules are small, in fact often negligible.^{9c}

Other generalized SCF methods include (c) Löwdin's²⁷ method,

which augments Eq. (68) with t_{ijk} , i.e. by keeping $\hat{U}_{ijk}$, etc., many-electron correlations in $\tilde{\chi}$ in addition to $\{\hat{f}_{ij}\}$'s and $\{\hat{U}_{ij}\}$'s, and (d) Slater's⁶¹ method. The latter is similar to (c); it makes i' , Eq. (67), self-consistent with the entire $\phi_0 + \chi$ without writing it out explicitly as in Eq. (20).

Thus, methods (c) and (d) include many-electron correlations ($n > 2$) and their effect on $\hat{f}_i$ through the generalized SCF procedure augmented even beyond the Brueckner method. In atoms and molecules, many-electron correlations are unimportant compared to pair correlations (see Section XVIII); their effect on $\hat{f}_i$ then will be even less important.

The generalized SCF methods (a) to (d) aim, therefore, at the expense of much theoretical and practical difficulty, at obtaining $\{\hat{f}_{ij}\}$, $\{\hat{U}_{ijk}\}$, etc., effects which are not significant to start with.

It will be easier to treat these $\{\hat{f}_{ij}\}$, $\{\hat{U}_{ijk}\}$, etc. as minor corrections to a theory based on the $\hat{u}_{ij}$'s alone, using the variation-perturbation approach.

B. Perturbation Theory

We mentioned above that the first-order R.S. equation (64) results if just that portion of $\tilde{E}$, Eq. (58), given in Eq. (63) is minimized. Equation (64) was solved rigorously⁸ by operator techniques starting with a H.F. ϕ_0 and gave

$$\chi_1 = \sum_{i>j}^N \frac{\mathcal{A}}{\sqrt{2!}} \left\{ (123 \dots N) \frac{\hat{u}_{ij}^{(1)}}{(ij)} \right\} \quad (69a)$$

$$\langle \hat{u}_{ij}^{(1)}, k \rangle = 0 \quad (k = 1, 2, \dots, i, \dots, j, \dots, N) \quad (69b)$$

The techniques will not be given here; they are discussed in detail elsewhere.^{8, 62, 63} $\hat{u}_{ij}^{(1)}$ are the correlations of all H.F. orbital pairs, to the first order only. They satisfy the equations^{8, 9b}

$$(e_i + e_j)\hat{u}_{ij}^{(1)} + Qg_{ij}\mathcal{B}(ij) = 0 \quad (70)$$

Q is the projection operator,^{9b} which "orbital-orthogonalizes" the two-electron function to the right of it to all k [hence Eq. (69b)]:

$$Q \equiv 1 - \sqrt{2} \sum_{k \geq 1}^N \mathcal{B}\{k\} \langle k \rangle + \sum_{l > k \geq 1}^N \mathcal{B}(kl) \langle \mathcal{B}(kl) \rangle \quad (71)$$

$$\langle QF(\mathbf{x}_i, \mathbf{x}_j), k(\mathbf{x}_i) \rangle_{\mathbf{x}_i} = 0$$

Aside from the "exclusion" and "medium" (V_i) effects of the larger H.F. "sea", Eq. (70) is analogous to the first-order equation of say the helium atom. We shall return below to details of Eq. (70) with respect to the symmetry properties within χ_1 , and its relation to the more "exact pairs" of the "many-electron theory".⁹

Note that Eq. (69) contains no $\{\hat{f}_i\}$, because

$$\langle \hat{u}_{ij}^{(1)}, i \rangle = \langle \hat{u}_{ij}^{(1)}, j \rangle = 0 \quad (72)$$

[see Eqs. (40) to (42)]. This is only true when ϕ_0 is H.F.* Had the i in ϕ_0 been hydrogen-like orbitals [$h_i^0 = \varepsilon_i^0 i$; Eq. (4a)] or Slater orbitals or simple LCAO MO's, etc., Eq. (72) would no longer hold.^{62,9c} Then the resulting $\hat{f}_i$, Eq. (41), would not represent just the effect of "correlation" on orbitals; they would mostly be "*orbital average polarization*"^{3,62} effects resulting from the remaining long-range parts of the interelectronic repulsions which are completely taken into account only in the H.F. ϕ_0 . Such $\hat{f}_i$ essentially try to modify the crude orbitals and turn them into the H.F. ones (see "Notes added in proof").

Perturbation theory has also been used in its usual infinite basis set expansion form starting with H.F.^{16,3} Nesbet¹⁶ uses E_2 , the second-order energy, to estimate the energy contributions in C.I. But the slow convergence^{1,3} of the C.I. expansions remains. A calculation on the methane molecule³⁸ with a gaussian basis set of eight orbitals gives only 1.95 ev, or roughly 26% of the correlation energy. This is relative to the crude H.F. energy, which itself has large errors, but the correlation energy calculated (20 configurations) should not be very sensitive to the crudeness of these ϕ_0 MO's. The results indicate that many more configurations may be needed to get the rest of the correlation energy.[†]

* In C.I. language this means that single excitations do not mix with the H.F. ϕ_0 ("Brillouin Theorem", see, e.g., Reference 1).

† Nesbet³⁸ chooses only those 20 configurations out of the several thousand possible that contribute more than 0.0005 a.u. each. The remaining configurations, however, could easily account for the remaining large correlation error (*ca.* 5 ev). Even if each configuration contributed $\sim 10^{-4}$ a.u., there being 10^{-3} of them, they would add up to ~ 3 ev. This slow convergence is the main difficulty with C.I.

The perturbation theory, Eqs. (69) to (71), on the other hand, is in a closed form and is not limited to an infinite C.I. expansion. (For applications to CH_4 , etc., see later sections.)

The perturbation results^{8,62} initially led us in a systematic way to the *form* of the more general and accurate “many-electron theory”⁹ (see below). However, as we have already pointed out, the final “many-electron theory” in no way necessitates the use of perturbation theory. It can be derived directly from Eq. (20). In fact, perturbation theory can be obtained from the “many-electron theory” upon further approximations, and for computations often provides a useful first approximation.³⁸

The perturbation result Eq. (69) is incomplete in two respects: (1) pair correlations are included only to the first order (in the w.f.); and (2) whether the other correlation effects $\hat{f}_i$, $\hat{U}_{ijk}$, $\hat{U}_{ijkl}$, . . . can truly be neglected is not considered except through the following convergence argument:

Comparing the perturbation series

$$\psi = \phi_0 + \chi_1 + \chi_2 + \dots \quad (73)$$

with Eqs. (20) and (69) we see that all effects other than $\hat{u}_{ij}^{(1)}$ must show up in χ_2 and higher orders. But χ_1 determines the energy through the third order [see Eq. (65)]. Then $\hat{f}_i$, $\hat{U}_{ijk}$, etc. can contribute to the energy only in the fourth and higher orders.

A measure⁹ of the convergence of Eq. (73) is

$$\langle \chi_1, \chi_1 \rangle / \langle \phi_0, \phi_0 \rangle = \langle \chi_1, \chi_1 \rangle \ll 1 \quad (74)$$

Also from Eq. (64) we have

$$\langle \chi_1, \chi_1 \rangle = \langle \chi_1, (H_0 - E_0)^{-1} (E_1 - H_1) \phi_0 \rangle \approx \frac{E_2}{E} \approx \frac{E_{\text{corr.}}}{E_{\text{total}}} \quad (75)$$

Thus $\langle \chi_1, \chi_1 \rangle$ is usually $\approx 1\%$ starting with H.F., the R.S. series therefore converges rapidly and χ_1 may be sufficient.

Higher order corrections to pair correlations, $\hat{u}_{ij}^{(2)}$, etc., also appear in χ_2, χ_3 , etc. This does not necessarily mean, however, that they contribute to the same extent as $\hat{f}_i$, $\hat{U}_{ijk}$, etc. All of these terms may be *formally* of the same “order” [in Eq. (73)], but their magnitudes may still differ greatly depending on

molecular geometry, the nature of the physical effect, and so on. An overall convergence argument, therefore, is not adequate in assessing the relative importance of physically different correlation effects.

These defects of the perturbation result⁸ are remedied in the "many-electron theory".⁹

C. "Many-Electron Theory"⁹

The generalized SCF methods,^{27,36,61} as well as the other non-empirical methods like C.I. discussed in Section IV, do not distinguish the major effects in χ and E from the minor ones.

By far, the largest effects in χ , Eq. (20), are the pair correlations, $\{\hat{U}_{ij}\}$. They should therefore be obtained as accurately as possible. The remaining effects need only be estimated, provided they are indeed small. In the forthcoming sections we shall obtain the pairs^{9b} "exactly" (i.e. to all "orders") from the major portions of the exact χ and the energy according to the "variation-perturbation" approach, and then examine and estimate the $\{\hat{f}_i\}$ ^{9c} and the many-electron effects^{9a} (Sections XIX and XVIII). Both in concept and practice, this leads to very simple results.

For convenience we continue the development on closed shell systems. Other systems are discussed in Sections XX and XXI. The theory is still based on non-localized H.F. orbitals and SCF MO's which satisfy Eqs. (12). The results are transformed into the localized description in Sections XXVII and XXVIII.

XVI. THE WAVE FUNCTION OF THE "MANY-ELECTRON THEORY"

The major part of the exact wave function χ , Eqs. (20), (50), etc., is the wave function

$$\chi_s = \sum_{i>j=1}^N \frac{\mathcal{A}}{\sqrt{2}} \left\{ (123 \dots N) \frac{\hat{u}_{ij}}{(ij)} \right\} \quad (76)$$

The $\hat{u}_{ij}$'s in it will be obtained (Section XXII) by minimizing a large portion of $\tilde{E}$ according to the variation-perturbation approach. They will then also give us estimates of the correction

terms $\{\hat{f}_i\}$, etc. Equation (76) has the same form as the perturbation result χ_1 , but in it the pairs are to all orders. These pair functions are denoted by lower case " $\hat{u}_{ij}$ "'s to distinguish them from the $\hat{U}_{ij}$'s of the exact wave function, Eq. (20). The latter depend implicitly on $\hat{f}_i$, $\hat{U}_{ijk}$, etc., whereas the $\hat{u}_{ij}$ of Eq. (76) are independent.

Once the $\hat{u}_{ij}$'s are known, a better w.f. than χ_s is obtained by including all their unlinked clusters. This is actually quite significant, since with χ_s alone we will get normalization terms in $\tilde{E}$, Eq. (58), $1 + \sum_{i>j}^N \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle$, which are of comparable magnitude to the effect of unlinked clusters. As discussed above these two effects tend to cancel out.

The complete w.f. of the many-electron theory^{9a} for closed shells is

$$\chi \approx \chi'_s = \mathcal{A} \left\{ (123 \dots N) \left[(2!)^{-\frac{1}{2}} \sum_{i>j}^N \frac{\hat{u}_{ij}}{(ij)} + (2!)^{-1} \sum_{i>j}^N \sum_{\substack{k>l \\ (i,j \neq k,l)}}^N \frac{\hat{u}_{ij} \hat{u}_{kl}}{(ijkl)} \right. \right. \\ \left. \left. + (2!)^{-\frac{3}{2}} \sum_{i>j}^N \sum_{\substack{k>l \\ (i,j \neq m,n \neq k,l)}}^N \sum_{m>n}^N \frac{\hat{u}_{ij} \hat{u}_{kl} \hat{u}_{mn}}{(ijklmn)} + \dots \right] \right\} \quad (77)$$

The prime on χ_s denotes that unlinked clusters are included. Note that in the products of the $\hat{u}_{ij}$'s, there are no indices in common (e.g. we have only $\hat{u}_{12} \hat{u}_{34}$, $\hat{u}_{13} \hat{u}_{24}$, etc.).

XVII. VARIATIONAL ENERGY OF THE "MANY-ELECTRON THEORY"

The terms that appear in the energy resulting from the above wave functions are easily found using the diagram technique defined in Sections IX and XIII. Take, for example, the χ_s first and substitute in the $\tilde{E}$ of Eq. (58). In each term use the fact that $\mathcal{A}$ commutes with

$$\sum_{i=1}^N e_i \quad \text{and} \quad \sum_{i>j}^N m_{ij}$$

and also Eq. (22). Draw a diagram for each "direct" term first, i.e. without the $\mathcal{A}$, then apply $\mathcal{A}$ in each diagram to get the corresponding exchange part. $\tilde{E}$ has been evaluated for both χ_s

and χ'_s . For the diagrams that result the reader is referred to Reference 9a. χ_s , Eq. (76), gives

$$E \leq E_s \equiv E_{\text{H.F.}} + \frac{\sum_{i>j}^N \tilde{\varepsilon}_{ij}}{D} + \frac{R}{D} \quad (78a)$$

$$\tilde{\varepsilon}_{ij} \equiv 2\langle \mathcal{B}(ij), m_{ij} \hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, (e_i + e_j + m_{ij}) \hat{u}_{ij} \rangle \quad (78b)$$

$$D \equiv 1 + \langle \chi_s, \chi_s \rangle = 1 + \sum_{i>j}^N \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle$$

The properties of the H.F. ϕ_0 make many of the diagrams^{9a} zero. For χ_s only, the remainder R contains the three-electron linked clusters

$$4 \sum_{ijk}^N \begin{array}{c} \text{---} \text{---} \text{---} \\ \text{---} \text{---} \text{---} \\ \text{---} \text{---} \text{---} \end{array} \quad (79)$$

which for this particular labeling, for example, means

$$\langle i \hat{u}_{kj}, m_{ji} \hat{u}_{ik} j \rangle \quad (80)$$

for the "direct" term.

Levine, Geller and Taylor⁶⁴ have discovered a non-zero exchange term in one diagram [Eq. (36)a of Reference 9a]; e.g.

$$\left(\begin{array}{c} \text{---} \text{---} \text{---} \\ \text{---} \text{---} \text{---} \end{array} \right)_{\text{exch.}} = \langle \hat{u}_{ij}, \hat{u}_{kl} \rangle \langle i l, g_{12} j k \rangle \quad (81)$$

This term is discussed in the next section.

With unlinked clusters many more diagrams arise.^{9a} The complete variational energy of the many-electron theory becomes, after the substitution of χ'_s , Eq. (77), in $\tilde{E}$, Eq. (58),

$$E \leq E'_s \equiv E_{\text{H.F.}} + \frac{\sum_{i>j}^N \tilde{\varepsilon}'_{ij}}{D'} + \frac{R'}{D'} \quad (82a)$$

$$\tilde{\varepsilon}'_{ij} \equiv \tilde{\varepsilon}_{ij} \frac{D_{ij}}{D'} \quad (82b)$$

$$\begin{aligned}
 D' &= 1 + \langle \chi'_s, \chi'_s \rangle \\
 &= 1 + \sum_{i>j}^N \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle + \sum_{i>j} \sum_{k>l} \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle \langle \hat{u}_{kl}, \hat{u}_{kl} \rangle + \dots
 \end{aligned} \tag{83}$$

$$D_{ij} = 1 + \sum_{\substack{k>l \\ (k,l \neq i,j)}} \langle \hat{u}_{kl}, \hat{u}_{kl} \rangle + \dots \tag{84}$$

D_{ij} contains all the pairs except the (ij) one. It arises^{51,9a} because the unlinked clusters in Eq. (77) give rise to factors $\langle \hat{u}_{kl}, \hat{u}_{kl} \rangle$ multiplying the ε_{ij} , Eq. (78b).

The many-electron diagrams that make up R' , in addition to those in R , Eq. (79), are shown in Reference 9a. They will not be needed here.

Note again that even though χ'_s contained only the pair correlations, in $\tilde{E}$ three-, four-, etc. electron effects also arose. These have been examined and found insignificant (Section XVIII).

According to the variation-perturbation approach we do not need to minimize the entire $\tilde{E}$'s, Eq. (82), to get the $\hat{u}_{ij}$'s. The major portion of the energy is

$$E_s'' \cong E_{\text{H.F.}} + \sum_{i>j}^N \tilde{\varepsilon}'_{ij} \tag{85}$$

where

$$\tilde{\varepsilon}'_{ij} \cong \frac{2\langle \mathcal{B}(ij), m_{ij} \hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, (e_i + e_j + m_{ij}) \hat{u}_{ij} \rangle}{1 + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \tag{86}$$

The ε'_{ij} in Eq. (82) reduces to Eq. (86) after the expansion of its denominator.^{9b} For example, in beryllium we have

$$\begin{aligned}
 \frac{D_{34}}{D'} &= \frac{1 + \langle \hat{u}_{12}, \hat{u}_{12} \rangle}{1 + \langle \hat{u}_{12}, \hat{u}_{12} \rangle + \langle \hat{u}_{34}, \hat{u}_{34} \rangle + \langle \hat{u}_{13}, \hat{u}_{13} \rangle + \dots} \\
 &\approx \frac{1}{1 + \langle \hat{u}_{34}, \hat{u}_{34} \rangle}
 \end{aligned}$$

Equation (85) forms a very good, usually "chemical" approximation (i.e. to about 1 kcal/mole) to E . It will be taken up again later as a basis for semi-empirical approaches. For non-empirical calculations, it is the part of Eq. (82) or (58) to be minimized in obtaining the $\hat{u}_{ij}$'s. Once the $\hat{u}_{ij}$'s are determined, substitution back into R' and D' gives an upper limit to the exact E and an estimate of the error involved in dropping these minor terms.

The next two sections examine the approximations made in arriving at χ'_s and E''_s , Eqs. (77) and (85), from the exact χ and $\tilde{E}$, Eqs. (20), (49)–(52) and (58).

XVIII. MANY-ELECTRON CORRELATIONS

Many-electron correlations, the *linked* clusters, appear (a) in the wave function χ as $\hat{U}_{ijk}$, $\hat{U}_{ijkl}$, etc., and (b) in the energy, Eq. (82), arising even from only the $\hat{u}_{ij}$'s. Both effects need to be examined.

The nature of electron correlation, the latter being defined as what is left over after Hartree–Fock, is determined by^{9a}

(i) the spatial distribution of electrons *relative to one another* in the H.F. “sea” as given by ϕ_0 ,

(ii) the pairwise “*fluctuation potentials*” $\sum_{i>j}^N m_{ij}$ [see $H - H_0$ and Eq. (17)] that cause electrons to “collide,” and

(iii) the effect of the exclusion principle on χ giving

$$\langle \hat{u}_{ij}, k \rangle = 0 \text{ with } k \neq i, j \text{ of } \phi_0 \quad (87)$$

A. Many-Electron Effects in the Wave Function

We discussed (i) in Section VII above. The relative distribution in ϕ_0 itself depends only on molecular geometry and on the Fermi holes between electrons of like spin, i.e. on the exclusion principle. The H.F. “sea” potential V_i makes the H.F. orbitals diffuse as compared to hydrogen-like ones for example, but its effect on “collisions” is indirect and faint (see below for the dependence of the $\hat{u}_{ij}$ on the overall “medium”).

Take *any* three electrons in an atom or molecule. At least two of these will have the same spin. We may find



or say



In (a), all the electrons stay away from each other owing to their Fermi holes, as given already by the ϕ_0 . No significant correction $\hat{U}_{ijk}$ appears in χ for such a three-electron same-spin "collision". Even the total correlation energy of $2p^3$ in the ^4S state of the nitrogen atom is only ≈ 0.1 ev (see Fig. 1),⁶⁷ most of which is due to the pairwise effect $\sum \varepsilon_{ij}$.

In (b) and all other cases involving even more electrons, at the most two electrons are allowed to approach each other in the "sea" ϕ_0 . For the two that come close together, a $\hat{u}_{ij}$ appears in χ .

This exclusion principle effect alone is not sufficient, however, to ensure the smallness of three or more electron Coulomb correlations. For instance, in (b) how far do the fluctuation potentials extend? Will m_{23} reach ③ for example? The $1/r_{23}$ itself, with its long range, would reach ③ but m_{23} would not. *The fluctuation potentials usually die out before reaching a third, fourth, etc., electron.*^{9a} The greater the localization of electrons in ϕ_0 , the shorter will be the range of m_{ij} between separately localized electrons.

This was demonstrated in Reference 9a for (1) electrons in two different concentric shells (Fig. 1 of Reference 9a) and (2) electrons in the same shell but in orbitals with different angular parts (Figs. 2 and 3 of Reference 9a).

For example, in the Be atom, the m_{ij} of 1s electrons dies out before reaching the H.F. Bohr radius of 2s electrons. This makes the intershell (1s2s) pair correlation small compared with that of $(1s)^2$, and the $(1s^2) \dots (2s)$ or $(1s^2) \dots (2s^2)$ three- or four-body correlations (linked ones) even smaller.

m_{ij} dies out even between electrons which occupy different orbitals but have the same principal quantum number. The fluctuation potential between $2p_z$ and 2s in boron is small just where the $2s^2$ correlation is large [within $\mp 45^\circ$ from the (xy) plane]. The reader is referred to Reference 9a for further details of the boron case. The behavior of the m_{ij} between p electrons in say C, N or Ne or of d electrons in A, etc. should be qualitatively similar to that in boron, making n -electron correlations ($n > 2$) of little importance even in large shells like $2p^6$ and $3d^{10}$.

A few available H.F. plus C.I. results did indeed confirm this picture. In the beryllium atom⁶⁵ and the lithium hydride molecule,⁶⁶ $3e^-$ correlations (triply excited configurations) turned out

to be totally insignificant. What appeared to be significant $4e^-$ correlations were later shown^{9a} to be just unlinked clusters. Their coefficients could be closely reproduced by multiplying the coefficients of independent pair excitations according to Eq. (55), showing that

$$\hat{U}'_{1234} \approx \frac{\mathcal{A}}{2} \{ \hat{u}_{12} \hat{u}_{34} + \hat{u}_{13} \hat{u}_{24} + \hat{u}_{14} \hat{u}_{23} \} \quad (88)$$

The Be results^{9a} are reproduced in Table Ia; similar results were found for the LiH molecule^{9a} (Table Ib). A more crucial non-empirical test of the theory would be on say the neon $2p^6$ shell, on which calculations are in progress.

TABLE Ia. Unlinked Clusters *vs.* Four-Electron Correlations in the Beryllium Atom

Quadruply excited configuration ^a	Coefficient from 37-configuration wave function ^a by full C.I.	Unlinked four-cluster coefficient calculated from pair correlation coefficients ^{b,c}
$p_{\text{I}}^2 (1S) \quad p_{\text{II}}^2 (1S)$	0.007063	0.0073
$p_{\text{I}}^2 (1S) \quad s_{\text{I}}^2 (1S)$	0.005651	0.00647
$p_{\text{I}}^2 (1S) \quad d_{\text{II}}^2 (1S)$	0.001585	0.00168
$p_{\text{II}}^2 (1S) \quad d_{\text{I}}^2 (1S)$	0.0004639	0.000478
Energy contribution	-0.075 eV ^d	-0.074 eV ^e

^a Watson, R. E., *Phys. Rev.* **119**, 170 (1960).

^b Section XVIII, Eq. (88), in text. Also Reference 9a.

^c The differences between the full C.I. coefficients and the unlinked cluster coefficients are due to the true four-electron correlations, $\hat{U}_{1234}$. They are very small.

^d From full C.I.^a

^e Calculated as $\epsilon_{ij} (1 - D_{ij})/D$ [compare Eqs. (78) and (82)]. The agreement with the full C.I. values shows that the true four-electron correlation terms appearing in R' are negligible.

The "exclusion effects" on χ , Eq. (87), also contribute to the smallness of n -body linked clusters. In fact, where electron localization is weak, e.g. in the benzene π -shell, this would be the main reason for expecting the many-electron terms to be small.

TABLE Ib. Unlinked Clusters *vs.* Four-Electron Correlations in the LiH molecule

Quadruply excited configuration ^a	Coefficient from full C.I. ^a	Unlinked four-cluster coefficient ^b
[3377]	0.00113	0.00113
[3357]	-0.00086	-0.00078
[3355]	0.00062	0.00052
[3456] ^c	$\begin{cases} -0.00023 \\ 0.00006 \end{cases}$	~ 0
[3457] ^c	$\begin{cases} 0.00014 \\ 0.00007 \end{cases}$	~ 0

Total $3e^-$ correlation energies < 0.01 ev

^a D. D. Ebbing, Ph.D. Thesis, Dept. of Chem., Indiana Univ., June, 1960. Configurations are in Ebbing's notation.

^b Section XVIII, Eq. (88), in text. Also Reference 9a.

^c These give two independent "codetors".

Equation (87) represents a $3e^-$ "Fermi correlation" between i , j and k . Electrons (spin-orbitals) i , j while correlating are prevented from making virtual transitions to spin-orbitals k which are already occupied. The more important a given k is in the C.I. expansion of $\hat{u}_{ij}$, the greater is this effect. Thus, as electrons become delocalized, near-degeneracies, and therefore the importance of certain of the k 's increase. This also makes their "exclusion effect"^{3,8,9} more significant.

For example, the $(1\sigma_g)^2$ correlation in H_2 is 7.74 ev at dissociation, where the MO's as such are delocalized and have to be corrected for by strong $(1\sigma_u)^2$ mixing.¹ The $(1\sigma_g)^2$ correlation energy in He_2^+ or (He—He), on the other hand, is *ca.* 0.5 to 1 ev, because now $(1\sigma_u)$ is occupied and therefore excluded. Then $(1\sigma_u)^2$ ceases to be the main part of $\hat{u}_{12}$. This type of 3 or $4e^-$ Fermi correlation is stronger than the corresponding coulombic correlations; therefore no significant $\hat{U}_{123}$ or $\hat{U}_{1234}$ appears in χ .

This argument cannot be applied indefinitely, however, as delocalization increases in larger and larger molecules, because in the end we reach metals and highly conjugated dye molecules in which collective screening and plasma effects appear.²⁶ In the

infinite electron gas²⁶ [positive uniform (+) background] lack of geometry offsets the "exclusion effect". Hartree-Fock orbitals become plane waves, $e^{ik\mathbf{r}}$, with the probability of an electron being anywhere in the box constant; also

$$m_{ij} \rightarrow 1/r_{ij}$$

as the box dimensions $L \rightarrow \infty$.^{9a} Many of the electrons can now "see" each other all at the same time and the H.F. ϕ_0 becomes an inadequate starting point.

B. Many-Electron Effects in the Energy

The properties of ϕ_0 , the m_{ij} , and Eq. (87) just described tend to make not only the $\hat{U}_{ijk} \dots n$ in χ , but also the many-electron terms R' in the energy, Eq. (82), small. Take the triangles, Eqs. (79) and (80), for example:

A given $\hat{u}_{ij}$ is large in space only where its $m_{ij}\mathcal{B}(ij)$ is also large [see Eqs. (86) and (70) and note that^{9b} $Qg_{ij}\mathcal{B}(ij) = Qm_{ij}\mathcal{B}(ij)$]. In a triangle term like Eq. (80) a product of $\hat{u}_{kj}$ with a different one, $\hat{u}_{ik}$, occurs. But owing to Eq. (87) (see, e.g., the boron case^{9a}) and the nature of the m_{ij} 's, wherever $\hat{u}_{kj}$ is large, $\hat{u}_{ik}$ is small and *vice versa*, making the product, and hence R , small everywhere.

These $3e^-$ contributions were estimated^{9a} from the C.I. results for Be⁶⁵ and LiH.⁶⁶ They came out^{9a} less than 0.01 ev in LiH. In Be, the only energy effect^{9a} of unlinked clusters was shown to come from D_{ij}/D [compare Eqs. (78) and (82); partial cancellation of normalization], showing that the rest of R' is also negligible (see Table I).

The largest of the new non-zero many-electron terms in Eq. (81) found by Levine, Geller and Taylor⁶⁴ is (in Be)

$$\langle \hat{u}_{12}, \hat{u}_{34} \rangle \langle 14, g_{12} 32 \rangle \quad (89)$$

where the last matrix element is $\langle 1s2s, g_{12} 2s1s \rangle$. Such terms are very easy to calculate. Only configurations (in C.I.) that contribute both to $\hat{u}_{12}$ and to $\hat{u}_{34}$ are retained in $\langle \hat{u}_{12}, \hat{u}_{34} \rangle$. Multiplying the coefficients of such configurations in Watson's⁶⁵ 37-term C.I. function, the writer and D. F. Tuan obtain

$$\langle \hat{u}_{12}, \hat{u}_{34} \rangle \cong 5.3 \times 10^{-4}$$

With the exchange integral derived from the ^1S and ^3S energies of Be^{2+} equal to 0.056 a.u., Eq. (89) $\cong 0.00081$ ev, an entirely negligible effect.

We showed that the nature of ϕ_0 and the exclusion principle tend to make both the $\hat{U}_{ijk\dots n}$ in χ and the many-electron terms R' in Eq. (82) which arise just from the $\hat{u}_{ij}$'s small. Computational evidence available so far supports this, and hence the working Eqs. (77) and (85) of the many-electron theory. Ways of calculating R' have been described in some detail^{9a,b} for further checks. It would be interesting to see the magnitudes of these terms, particularly in large π -electron systems.

The main many-electron effects in the energy appear in R , Eqs. (78a) and (79). The $\hat{U}_{ijk}, \hat{U}_{ijkl}, \dots$ of χ should contribute less to the energy; in perturbation theory they give higher order corrections. It seems sufficient therefore to estimate only R .

For non-empirical calculations it is not necessary that R' be entirely negligible. It only has to be smaller than $[\sum_{i>j}^N \tilde{\epsilon}'_{ij}]$. The variation-perturbation procedure then applies. The larger $\Sigma \tilde{\epsilon}'_{ij}$ part gives the $\hat{u}_{ij}$'s, which in turn determine R' .

R' may often be neglected, however. Equation (85) then shows the additivity of *uncoupled* pair correlations. This is important for the semi-empirical theories of spectra as discussed in Sections XXIV and XXVI.

Equation (85) has been confirmed very recently⁶⁷ for the first row atoms (Gladney and Allen⁶⁸ later obtained similar empirical values). Clementi⁶⁷ evaluated the correlation energies of these atoms and their ions empirically using his H.F. results and estimates of relativistic effects. The additivity observed is within the empirical uncertainty of the data. Figures 1 and 2 are based on his data and show the correlation energy increments in nitrogen and neon ions and atoms as more and more electrons are added.

XIX. EFFECT OF CORRELATION ON ORBITALS, $\hat{f}_i$

We saw that in closed shells many-electron correlations are unimportant and that the $\hat{u}_{ij}$ have a quite local, short-range character, becoming large only when two electrons are close together. This means that in spite of appreciable shifts in energy

due to correlation, the overall electron density will not be affected much.

Whether H.F. orbitals are the best ones to use or whether one

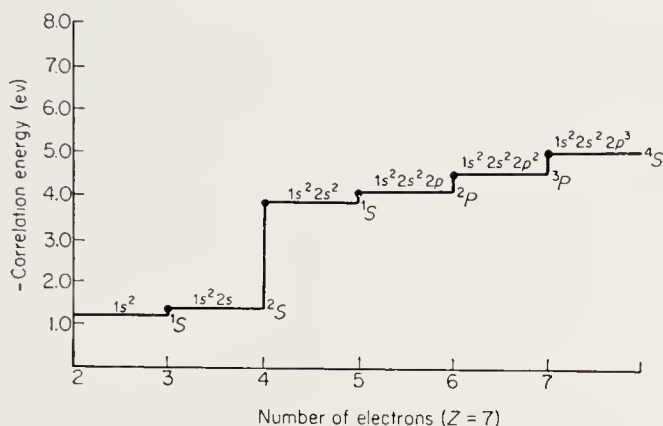


Fig. 1. Correlation energies of nitrogen ions and atom (based on the empirical data of E. Clementi, Reference 67).

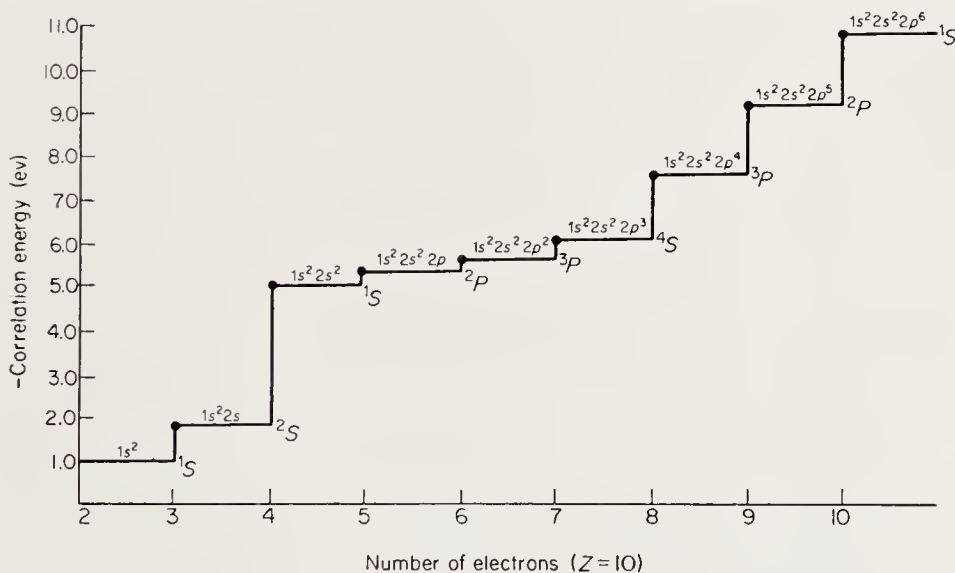


Fig. 2. Correlation energies of neon ions and atom (based on the empirical data of E. Clementi, Reference 67).

should go on to a generalized SCF method depends on how small the $\hat{f}_i$ are. Qualitative quantum chemistry has to be based on an orbital description and so this question of whether $\hat{f}_i$ are necessary is of particular importance.

The physical significance of $\hat{f}_i$ has been examined in great detail and its magnitude estimated for some typical cases.^{9c}

Correlation effects may be divided into “dynamical” and “non-dynamical” ones.^{69,9c} Dynamical correlation occurs with a “tight pair” of electrons as in He or the $(2p_z)^2$ in Ne, etc. There is no one configuration in χ which mixes strongly with ϕ_0 and C.I. is slowly convergent. “Non-dynamical” correlations,⁶⁹ on the other hand, arise from degeneracies or near-degeneracies (first order C.I.).⁶ In this section we shall be concerned with $\hat{f}_i$ resulting from dynamical correlations. $\hat{f}_i$ resulting from degeneracies, such as in non-closed shells, or from near-degeneracies are discussed in Sections XX and XXI.

“Dynamical” $\hat{f}_i$ are expected to be small.^{9c} Aside from the perturbation theory arguments given in Section XV-B, other reasons for this expectation are: (a) observed X-ray electron densities⁷⁰ are close to those calculated from H.F. orbitals, (b) C.I. calculations, e.g. Watson’s⁶⁵ calculation on Be, show negligible effects from single excitations [see Eq. (45)], (c) long-range Coulomb repulsions are mainly in ϕ_0 ; the $\hat{f}_i$ ’s arise from “spreading thin” the effects of local “collisions”, $\hat{u}_{ij}$ [see, e.g., Eq. (41)], over an entire orbital, and (d) direct calculations^{9c} in closed form also give small $\hat{f}_i$.

The exact $\hat{f}_i$ are given by Eq. (28). Thus, in principle, all parts of χ , two as well as $n > 2$ correlations, contribute to $\hat{f}_i$. The many-electron terms ($n > 2$), however, are small to start with, and hence their effect on $\hat{f}_i$ will be even smaller.

Equation (28) shows how to calculate $\hat{f}_i$. Suppose one has a good trial function $\tilde{\psi}$ in which no correlation effect and not even the Hartree-Fock part is explicit. Such a $\tilde{\psi}$ can be analyzed by the “method of partial orthogonalizations” according to Eqs. (26) through (36). After the $\tilde{\chi}$ is separated, Eq. (28) gives the $\hat{f}_i$.

For a He atom one has Eqs. (39) and (41). Similarly, for a many-electron system, Eq. (28) reduces to

$$\hat{f}_i \cong \sqrt{2} \sum_{j \neq i}^N \langle u_{ij}, i \rangle_{\mathbf{x}_i} \quad (90)$$

where $\langle u_{ij}, k \rangle = 0$ for $k \neq i, j$ and n -electron correlations ($n > 2$) have been neglected. Thus, one simply has to look at the different types of pairs in the many-electron system, obtain their u_{ij} as

shown in Section XXII by splitting off their $\mathcal{B}(ij)$ parts and putting in the exclusion effects and then get the corresponding $\hat{f}_i$ contribution from Eq. (90).

In He, $\hat{f}_i$ was calculated^{9c} with ψ 's containing r_{12} .

Suppose now that a trial function gives a non-negligible $\hat{f}_i$. Does this mean that $\hat{f}_i$ in the exact χ is not small or does it mean that the trial function was poor and introduced an artificial $\hat{f}_i$? If the latter is the case, one should get a better trial function, i.e. one giving a lower energy, by taking out the $\hat{f}_i$ part.

The "scaled"¹ Löwdin and Redei^{1,73} function of He

$$\tilde{\psi}(\mathbf{r}_1, \mathbf{r}_2) = \mathcal{N}(1 + \eta\alpha r_{12})u(\eta r_1)u(\eta r_2) \quad (91)$$

where the u are two exponential analytic SCF orbitals, η is the "scaling"¹ parameter and α is a variational one, gives 80% of the correlation energy. Its $\hat{f}_i$ part,^{9c} plotted in Fig. 3, is largest (about 5% of the H.F. orbital there) at the nucleus. When these $\hat{f}_i$ parts are taken out so that $\tilde{\psi}$ reduces to

$$\mathcal{B}(12) + \hat{u}_{12} \quad (92)$$

according to Eqs. (40) and (49), the energy is lowered by 0.019 ev or 1.7% of $E_{\text{corr.}}$.

Further evidence for the smallness of $\hat{f}_i$ in the exact χ of He comes from a better trial function. Hylleraas'⁷⁴ six-term wave function (98% of the correlation energy) gives^{9c} much less $\hat{f}_i$ (Fig. 3). This $\hat{f}_i$ is apparently a real effect, since when it is taken out the energy is *raised* by 0.24% of $E_{\text{corr.}}$, which, however, is negligibly small (63 cal/mole). Similar results are found^{77,78,9c} for the H_2 molecule near the equilibrium distance r_e . (For H_2 near dissociation see Section XXI.^{9c})

Other pairs with dynamical correlation, e.g. the inner shells of molecules, the $(2p_z)^2$ pair in Ne, etc., should give similarly negligible $\hat{f}_i$. Intershell pairs,^{3,4} e.g. $(1s2s)$, have small $\hat{u}_{ij}$'s which are approximated very well by perturbation theory [$\hat{u}_{ij}^{(1)}$ in Eq. (69a)], and hence contain no $\hat{f}_i$. Several other cases are discussed in Reference 9c.

The unimportance of $\hat{f}_i$ (see also Sections XX and XXI), along with that of many-electron correlations, means that:

(i) Hartree-Fock orbitals, e.g. MO SCF, provide a valid description for most aspects of quantum chemistry.⁴³ Correlation does

not change the qualitative pictures based on ϕ_0 (such as those of Lennard-Jones, Pople and Linnett; see also footnote on pages 325 and 326).^{35a,35b,35c}



Fig. 3. $\hat{f}_i$ in He atom (Reference 9c). $\hat{f}_i$ represents the modification that correlation introduces on top of the Hartree-Fock orbital, $1s$. The new orbital would have been $(1 + \hat{f}_1)/\sqrt{1 + \langle \hat{f}_1, \hat{f}_1 \rangle}$, but $\hat{f}_1$ can be neglected. Thus H.F.SCF alone gives good orbitals. $(- (2) - -)$: $\hat{f}_1$ calculated from the scaled Löwdin and Redei function (Eq. 91) in text. $(- (1) -)$: $\hat{f}_1$ from Hylleraas' six-term wave function (see Section XIX).

(ii) Correlation effects can be separated into shells according to Eq. (85). This would not have been possible had $\hat{f}_i$ contained long-range coulombic effects.*

* Szász's work²⁵ did not separate the $\hat{f}_i$, but put these and the many-electron effects on the same footing as u_{ij} . It therefore did not bring in the shell picture and the computational and theoretical advantages arising from it.

(iii) The theory is greatly simplified, because not only the $\hat{f}_i$ but also their many unlinked clusters [Eqs. (49)–(55)] drop out. This makes the complications that Brueckner-type generalized SCF theories would introduce unnecessary. One may still estimate the $\hat{f}_i$, but being small they do not have to be made self-consistent with the $\hat{u}_{ij}$'s.

XX. NON-CLOSED SHELLS

In the above Sections, the exact χ and E , as well as the many-electron theory, were formulated and many-electron effects and $\hat{f}_i$ were examined mainly for closed shells. This was to avoid a very general and complicated notation. The theory of non-closed shells requires few modifications.

The Hartree–Fock part of ψ was discussed in Section VI. The *form* of the exact wave function for a non-closed shell system is the same as Eq. (20). ϕ_0 , the *entire* H.F. part, will in general be a linear combination of several Slater determinants (“codetors”), ϕ_i

$$\phi_0 = \sum_{i=1}^M \phi_i \quad (93)$$

The complete C.I. series for the exact ψ contains all the “ordered”, unique Slater determinants that can be formed from a complete one-electron basis set. In the case of closed shells and also for non-closed shell states of high multiplicity, a single determinant is a symmetry eigenfunction (e.g. in atoms of L^2, S^2, L_z, S_z as well as of H_0). There is no degeneracy and this single determinant occurs in the C.I. series with by far the largest coefficient. All the other determinants account for “dynamical correlation” in the slowly convergent way discussed previously. Thus the above theory applies to single determinant non-closed shell states such as ^2S lithium, ^2P boron, ^3P carbon, ^4S nitrogen, ^3P oxygen, ^2P fluorine, etc., just as it did to the closed shell states, provided the H.F. orbitals have been obtained by minimizing the energy of that particular determinant.

In other states, such as the ^1S of C ($1s^2 2s^2 2p^2$), several degenerate codetors with equally large coefficients occur in the complete C.I. series of ψ .* In such cases, ψ can be split into an “H.F.” and a

* For tables and the construction of determinantal eigenfunctions of atoms see, for example, Slater.¹⁷

“correlation” part in several ways corresponding to the various possible H.F. methods mentioned before.

The exact ψ is

$$\psi = \phi_0 + \chi = \sum_{i \geq 1}^M c_i \phi_i + \sum_{j > M}^{\infty} c_j \phi_j \quad (94)$$

where the ϕ_i are the M degenerate determinants and the ϕ_j all the other determinants that make up the exact χ . The first sum represents the ϕ_0 , the second one the χ . Thus here $\langle \chi, \phi_i \rangle = 0$. The χ of course need not be written in C.I. form.

In one approach one splits the exact ψ , Eq. (94), as follows:

$$\psi = c_1 \phi_1 + \sum_{L > 1}^{\infty} c_L \phi_L \quad (95)$$

and obtains the H.F. “sea” orbitals from just a single determinant ϕ_1 as in the “unrestricted H.F.” method.³¹ Then “correlation” will contain degeneracy effects, Eq. (93), which are taken care of by first-order C.I.,⁶ in addition to “dynamical” effects. This viewpoint taken by Nesbet⁵ has definite computational advantages when Eq. (93) contains too many determinants as in the N_2 molecule near dissociation.⁵ The disadvantage is, however, that the physically different “dynamical” and “non-dynamical” correlations are not separated. Equation (95) gives seemingly large many-electron “correlations” and quite significant $\hat{f}_i$, which however actually come from just the Eq. (93) part, which is not as difficult to handle as the “dynamical” part.

The other approach splits ψ as in Eq. (94) and obtains the occupied orbitals from the entire equation (93) (“Extended” H.F.).^{1,75} Thus the first-order C.I. or “degeneracy” effects which still involve the long-range parts of Coulomb repulsions and the overall charge distributions are attributed to the Hartree–Fock ϕ_0 . Once this is done, the last sum of Eq. (94) contains only the “dynamical correlations”, to which all the arguments given above for closed shells apply. Then “many-electron correlations” and the $\hat{f}_i$ will be small. “Correlations” so defined will be pairwise-additive. Clementi’s⁶⁷ results on first row atoms which include non-closed shell states confirm this. His H.F. is of the

“extended” type; new orbitals are obtained for each non-closed shell state.

The “extended H.F.” may be viewed as a generalized SCF method²⁷ in which orbitals, say of ϕ_1 in Eq. (95), are being made self-consistent with *only the degeneracy type correlations*. But generalized SCF methods like Brueckner’s, attempt to adjust the orbitals not only to the “first-order C.I.” effects, but also to the “dynamical” correlations, i.e. to the infinite sums in Eq. (94) or (95), as well. Dynamical correlations are the ones that give rise to difficulties in a generalized SCF method. On the other hand, they are the ones that do not necessitate such an SCF procedure because the “dynamical” f_i are small anyway.

The [“extended H.F.” + *dynamical correlations*] approach, though an accurate method, requires that new orbitals be calculated for each non-closed shell state arising from say the same atomic configuration.

The H.F. method based on the “average energy of a configuration with restrictions” is a compromise. Again ψ is split as in Eqs. (93) and (94), but the H.F. orbitals are obtained in the way described in Section VI, so that they are the same say for the ^3P , ^1D and ^1S of the C ($1s^2 2s^2 2p^2$) atom. With this H.F. most of the last sum in Eq. (94) is “dynamical correlation”, i.e. in the form of Eq. (77). There will also be some f_i which try to turn the “average” orbitals of this type of ϕ_0 into those of “extended H.F.”. We mentioned that the energy change due to these f_i in atoms and small stable molecules is usually less than 0.01 ev (Section VI) as judged from comparisons of different types of H.F. calculations.

Thus, for most non-closed shells many-electron theory in the form of Eqs. (77) and (85) may be safely assumed to apply with H.F. based on the “average energy of the non-closed configuration with restrictions”. With this H.F., the perturbation equation (64) can again be solved by operator techniques. Having V_i the same for all the electrons simplifies matters; also one notes that the projection operators that turn say ϕ_1 into ϕ_0 in Eq. (93) commute with $\mathcal{A}$, H_0 and H_1 . Löwdin’s projection operators⁷⁵ should be useful in applying the many-electron theory⁹ and the perturbation theory⁸ to non-closed shells.

XXI. NEAR-DEGENERACY

We have seen how the many-electron theory can be applied to closed and to non-closed shell systems. Systems with near-degeneracies, however, fall between these two classifications. Two important causes of such near-degeneracy were cited in Section VI: (a) in atoms degeneracies arise as $Z \rightarrow \infty$; and (b) near-degeneracies arise in molecules near dissociation. How far can these systems be treated as closed shells with a single determinant ϕ_0 and negligible f_i ?

(a) A well studied^{34,65} example of Z -degeneracy occurs in the Be isoelectronic series. Even in Be, C.I. study⁶⁵ shows that the correlation error in the outer shell comes mainly from the strong $2s^2$ - $2p^2$ mixing. The $2p^2$ coefficient⁶⁵ is -0.297 if the coefficient of $2s^2$ is taken as 1.000 . In the series Be, B^+ , C^{2+} , N^{3+} . . . this correlation effect turns out³⁴ to be linear in Z . (For the Z -dependence of this correlation in atoms with more than four electrons see Section XXIV.)

This large $2p^2$ mixing can apparently still be considered as part of χ , and the H.F. calculation can be based on the $1s^2 2s^2$ configuration alone, as evidenced by the entirely negligible single excitation effects (f_i) found by Watson.⁶⁵ Kibartas *et al.*⁷⁶ have also done an "extended" SCF calculation on the $1s^2 2s^2$, $1s^2 2p^2$ and $2s^2 2p^2$ combination for Be. Their results differ from H.F. on $1s^2 2s^2$, followed by $1s^2 2s^2$ $1s^2 2p^2$ two-by-two C.I.,³⁴ by about 0.001 a.u. (0.027 ev), showing the f_i effect to be quite small again.

(b) Near-degeneracies in dissociating diatomic molecules are of particular importance in the theory of interatomic forces. Consider, for example, the H_2 molecule.

At the equilibrium internuclear distance $r = r_e$ (0.74 Å) the H_2 correlation is of the "dynamical" type, very similar to that of the He atom. Hartree-Fock is based on $(1\sigma_g)^2$ and gives an $E_{\text{corr.}}$ of -1.06 ev.¹ Davidson and Jones⁷⁷ have calculated the f_i for H_2 at $r = r_e$ from the Kolos-Roothaan wave function⁷⁸ and found it to be negligible, as in the case of He.^{9c} (They consider the difference between H.F. and *natural orbitals*. f_i is a first approximation to the difference.)

At $r = \infty$, if H.F. is still based on $(1\sigma_g)^2$, the molecule does not dissociate into two $(1s)$ hydrogen atoms; a "correlation" error of

7.74 eV results.¹ This, however, is strictly a degeneracy effect. A two-by-two (first-order) C.I. between $(1\sigma_g)^2$ and $(1\sigma_u)^2$ degenerate with it removes most of the error. So, at $r = \infty$ we have the non-closed shell problem with dynamical correlation missing.

This degeneracy-type non-dynamical correlation introduces a non-negligible $\hat{f}_i$ at $r = \infty$. This has been obtained^{9c} by comparing

TABLE II. Estimated Energy Lowering due to the Inclusion of Single Excitations⁷⁹ or $\hat{f}_i$ in the H_2 Molecule ($r = \infty$ case is calculated in a different way than for other values; see text and References 9c, 79 and 1)

Internuclear distance r , a.u.	Energy contribution of $\hat{f}_i$ or single excitations, eV
∞	-0.4
12.0	-0.33
4.0	-0.32
3.0	-0.13
2.0	-0.027
1.4 ($\sim r_e$)	-0.0092
1.1	-0.0046

the exact ψ , which is just the symmetrized $(1s_a 1s_b)$, with the $(1\sigma_g)^2$ H.F. of Löwdin¹ followed by C.I. with $(1\sigma_u)^2$. The energy contribution from the $\hat{f}_i$ part is *ca.* 0.4 eV.^{9c}

Fraga and Ransil⁷⁹ studied H_2 by $(1\sigma_g)^2$ H.F. followed by C.I. for $1.0 \leq r \leq 12.0$ (a.u.). They used a limited LCAOMO SCF with $1s$, $2s$, $2p$ in the basis set and included twelve configurations. Of these $(1\sigma_g 2\sigma_g)$ and $(1\sigma_g 3\sigma_g)$ are single excitations and correspond to the first terms in the C.I. expansion of $\hat{f}_i$. From the coefficients which Fraga and Ransil give, and a perturbation procedure proved by Neil R. Kestner (see Appendix of Reference 9c), the energy contributions of these single excitations have been estimated^{9c} for $12.0 \leq r \leq 1.1$ (a.u.). These values, given in Table II, show how $\hat{f}_i$ varies with r . If 0.1 eV is considered a small error, the $\hat{f}_i$ effect is negligible for $(r/r_e) < 2$.

Thus at $(r/r_e) < 2$, the correlation is dynamical with

$$\psi \cong \mathcal{B}(12) + \hat{u}_{12}$$

as in He. At larger r , $\{\hat{f}_i\}$ also come in owing to non-dynamical correlation. They can be introduced either as additional perturbations or by going over to "extended" H.F.

The H_2 example indicates that in intermediate cases, the $\hat{f}_i$ may be examined and the starting ϕ_0 decided upon. Fortunately, this problem does not come up in obtaining most binding energies ($r = r_e$) and in non-bonded interactions. For example, the composite system of two Ne atoms (starting with MO's) remains a single determinant at all r owing to "exclusion effects". The many-electron theory for closed shells can also be applied to this system as well as to non-bonded interactions between the bonds of say a saturated hydrocarbon (see Sections XXVII and XXVIII).

XXII. PAIR CORRELATIONS

Sections XVI through XXI show that after degeneracies are removed the main effects are the pair correlations, $\hat{u}_{ij}$, Eqs. (77) and (82) or (85). These are now to be obtained according to the variation-perturbation procedure by minimizing a large portion of $\tilde{E}$, Eq. (82). Once determined they will also give estimates of $\hat{f}_i$ and R' . Properties of pair functions, their relation to the states of actual, free two-electron systems and methods for their evaluation have been given in detail previously.^{9b} The results are summarized here.

According to Eq. (85) the pairs are decoupled. There may be some symmetry relations between different u_{ij} 's as discussed in Section XXIII below, but otherwise they are independent. An independent ε'_{ij} has just the form of the variational energy of an actual two-electron system, say a He atom. Using Eqs. (18) and (19) or (39) and (37) or (58) one has, for instance, for the He atom

$$E_{\text{He atom}} = E_{\text{H.F.}} + \frac{2\langle \mathcal{B}(12), m_{12} u_{12}^0 \rangle + \langle u_{12}^0, (e_1 + e_2 + m_{12}) u_{12}^0 \rangle}{1 + \langle u_{12}^0, u_{12}^0 \rangle} \quad (96)$$

We have also shown in Section XIX that

$$u_{12}^0 \cong \hat{u}_{12} \quad (97)$$

[see Eqs. (40), (49) and (92)].

An electron pair ε'_{ij} , Eq. (86), within the N -electron H.F. "sea" (e.g. the $1s^2$ core in Ne) differs from a free two-electron system,

e.g. the Ne^{8+} ion, in (i) the “exclusion effects” and (ii) the fact that V_i comes from all the N electrons instead of just from the two electrons of the pair (see also Section XIII).

The effective Schrödinger equation of the pair in the “sea” is obtained by varying an independent ε'_{ij} with respect to $\hat{u}_{ij}$, but subject to^{9b}

$$\langle \hat{u}_{ij}, k \rangle = 0 \quad (k = 1, 2, \dots, i, \dots, j, \dots, N)$$

This variation is easily carried out by noting that Q in Eq. (71) is Hermitian and idempotent

$$Q^2 = Q \quad (98)$$

and rewriting Eq. (86) as

$$\tilde{\varepsilon}'_{ij} = \frac{2\langle Qm_{ij}\mathcal{B}(ij), \hat{u}_{ij} \rangle + \langle Q(e_i + e_j + m_{ij})\hat{u}_{ij}, \hat{u}_{ij} \rangle}{1 + 2\langle Q\mathcal{B}(ij), \hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, \hat{u}_{ij} \rangle} \quad (99a)$$

The arbitrary variations $\delta\hat{u}_{ij}$ then automatically remain as $Q\delta\hat{u}_{ij}$, i.e. “orbital orthogonal” to all the k of ϕ_0

$$\langle Q\delta\hat{u}_{ij}, k \rangle = 0 \quad (99b)$$

The result is

$$(e_i + e_j)\hat{u}_{ij} + Qm_{ij}[\mathcal{B}(ij) + \hat{u}_{ij}] = \varepsilon_{ij}\hat{u}_{ij} \quad (100a)$$

with ε_{ij} the stationary value of $\tilde{\varepsilon}'_{ij}$

$$\varepsilon_{ij} \equiv \langle \mathcal{B}(ij), g_{ij}\hat{u}_{ij} \rangle \quad (101)$$

Equation (100) is the effective Schrödinger equation [compare Eqs. (2) and (62)]:

$$H_{ij}\hat{\psi}_{ij} = E_{ij}\hat{\psi}_{ij} \quad (102a)$$

with

$$E_{ij} \equiv \varepsilon_i + \varepsilon_j - J_{ij} + K''_{ij} + \eta_{ij} \quad (102b)$$

and $\hat{\psi}_{ij} \equiv \mathcal{B}(ij) + \hat{u}_{ij}$. We have combined the H.F. part with the correlation part, Eq. (100), in arriving at Eq. (102a).

If just the

$$2\langle Q\mathcal{B}(ij), m_{ij}\hat{u}_{ij} \rangle + \langle \hat{u}_{ij}, (e_i + e_j)\hat{u}_{ij} \rangle \quad (103)$$

portion of Eq. (86) is varied one gets the first order part [Eq. (70)] of Eq. (100).

If the entire numerator of $\tilde{\varepsilon}'_{ij}$ is varied one gets

$$(e_i + e_j + Qm_{ij})\hat{p}_{ij} = 0 \quad (100b)$$

This is similar to the closed form^{9b} of the Bethe–Goldstone equation for finite nuclei.⁸⁰ The latter is, however, for particles *in the Brueckner “sea”* instead of the H.F. “sea” represented by the V_i of Eq. (103). A Bethe–Goldstone type equation in a form which would be useful for actual calculations on finite nuclei, the properties of its solutions and its variational principle are given in the Appendix of Reference 9b.

Note that both Eq. (70) and Eq. (103) approximate to those solutions of Eq. (100) for which $\langle \hat{u}_{ij}, \hat{u}_{ij} \rangle \ll 1$. These approximate forms are valid for solutions corresponding to small correlation shifts from $\mathcal{B}(ij)$.^{9b}

Equation (100), (70) or (103) can sometimes be solved directly, though approximately, as in the core polarization method^{3,4} for some inter-shell correlations (see Section XXIV). But, in general, as for the He atom, we need variational methods to obtain the $\hat{u}_{ij}$.

Minimum principles: The solutions of the effective Schrödinger equations (100) or their approximate forms Eqs. (70) and (103) make the corresponding $\tilde{\varepsilon}'_{ij}$'s stationary. But most of the pairs, e.g. $2s^2$ in Be, $2p_z^2$ in Ne, etc., are in outer shells and are similar to “excited” pair states. The difficulties of applying the variation method to actual excited states are well known. Outer shells, when minimized, usually converge to the innermost shell.⁸⁸ This difficulty does not appear in the many-electron theory, i.e. in $\tilde{\varepsilon}'_{ij}$, however. A practical variation method, i.e. a minimum principle, applies to *any* pair $\hat{u}_{ij}$.

It is easily shown^{9b} that *each $\tilde{\varepsilon}'_{ij}$ is not only stationary but it is individually a minimum*. Thus, one simply needs to *minimize* Eq. (86) or (99a) or its portions *subject to* Eq. (99b) using trial functions $\hat{u}_{ij}$ to approximate the solutions of the corresponding differential equations.

This allows one to deal with the outer shells only, e.g. as in Na_2 or BaO or the π -electron part of benzene, etc., without converging to the inner shells.^{9b}

When the level scheme given by H.F. orbitals is in a one-to-one correspondence with the experimental one, Eqs. (70) and (103) give the “adiabatic” shifts due to $\hat{u}_{ij}$. On the other hand, if

the level scheme is not known, as in the breakdown of Hund's rules in some non-closed shells, Eqs. (100) and not Eq. (70) or (103) must be used; for instance, Eqs. (100) automatically pick the ground state. *Orbitals give the correct level scheme if the minimum of each $\tilde{\epsilon}'_{ij}$ occurs for those values of the variational parameters which also make $\langle \hat{u}_{ij}, \hat{u}_{ij} \rangle$ smallest compared to unity.* (See also the discussion which follows Eq. (47) of Reference 9c.)

Any of the methods available for actual two-electron systems¹ like He or H₂ can be used to obtain trial functions for our $\hat{u}_{ij}$ pairs. Different pairs of the N -electron system are physically quite different so that there is no one method which is convenient and suitable for all the pairs. For instance, the " r_{12} -coordinate" method would be appropriate for a $1s^2$ inner shell or the $(2p_z)^2$ pair in Ne, but not necessarily for $1s2s$. In particular, the use of the " r_{12} -coordinate" method for all the pairs of the entire^{46,48b} χ_s may introduce unnecessary mathematical difficulties. The types of pair methods that may be used and further details on how to use them are given below in building up all the first row atoms and their ions step by step (Section XXIV).

For use in the context of the many-electron theory, the wave function ψ_{ij} (ordinarily normalized to unity) of any two-electron method must first be written as

$$\psi'_{ij} = \mathcal{B}(ij) + u_{ij}^o; \quad \langle \mathcal{B}(ij), u_{ij}^o \rangle = 0 \quad (104)$$

by a change of normalization. That is

$$\langle \psi_{ij}, \psi_{ij} \rangle = 1 \quad \text{but} \quad \langle \psi'_{ij}, \psi'_{ij} \rangle = 1 + \langle u_{ij}^o, u_{ij}^o \rangle \quad (105)$$

This is done according to

$$\begin{aligned} \psi_{ij} &= c\psi'_{ij}; & c &\equiv \langle \psi_{ij}, \mathcal{B}(ij) \rangle \\ u_{ij}^o &= \frac{1}{c} [\psi_{ij} - c\mathcal{B}(ij)] \end{aligned} \quad (106)$$

Note that $\mathcal{B}(ij)$ are two *H.F. spin-orbitals picked out of the entire N -electron ϕ_0* for that particular pair. They are *not* the orbitals of a free $2e^-$ system.^{9b}

The u_{ij}^o obtained from Eq. (106) are next made orthogonal to all the k of ϕ_0 using Q , Eq. (71). Integrations are usually straightforward.

For an N -electron system, the χ of Eq. (69a), (76) or (77) contains $\frac{1}{2}N(N-1)$ $\hat{u}_{ij}$'s. Many of these differ, however, only in their orientation in space or their spin [e.g. the $(2p_x)^2$ pair in Ne is the same as the $(2p_y)^2$ pair and so on]. The number of distinct^{8,9b,62} $\hat{u}_{ij}$'s to be determined is, then, of the order of N . This can be seen from the symmetry properties of χ discussed in the next section. Only these unique pairs need to be determined. Some methods for their determination are given in Section XXIV.

XXIII. SYMMETRY PROPERTIES

χ , χ_s and χ'_s must have the same symmetry as ϕ_0 ; for instance, in Ne they must all be ^1S . Do χ_1 , χ_s or χ'_s satisfy this requirement, and if so what restrictions does this place on the $\hat{u}_{ij}$'s?

χ_s , Eq. (76), has the same form as χ_1 , Eq. (69), and it has the same types of pairs in it, but to all "orders". Recall that χ_1 was obtained by rigorously solving^{8,62} Eq. (64). This rigorous solution ensured that χ_1 had the same symmetry as ϕ_0 . This is because if ϕ_0 is ^1S in Eq. (64), $(H_0 - E_0)$ and $(E_1 - H_1)\phi_0$ will also have the same ^1S symmetry. This makes the solution χ_1 ^1S as well.

Previous derivations^{8,62} of χ_1 were made so that the pairs were related to the different states of an *actual free* two-electron system. The antisymmetrizer $\mathcal{A}$ in Eq. (64) allowed the $\mathcal{B}(ij)$'s to be transformed into pair states belonging to the irreducible representations of the two-electron symmetry group.^{9b} This showed, for example, that even though $\frac{1}{2}N(N-1)$ is 6 in Be, there are only four independent $\hat{u}_{ij}$'s distinct in their spatial part: $1s^2^1S$, $2s^2^1S$, $(1s2s)^1S$, and ^3S . Three of the six pairs are the different S_z components of ^3S . Similarly, in the $2p^6$ shell of Ne, $\frac{1}{2}N(N-1) = 15$, but there are only three distinct pairs:

$$2p^2\ ^3P, 2p^2\ ^1D \text{ and } 2p^2\ ^1S.$$

The transformation of $\mathcal{B}(ij)$ type pairs into these "irreducible pairs" was needed if one obtained the $u_{ij}^{(1)}$'s from the first-order $2e^-$ equations *without* the exclusion effects

$$\langle \hat{u}_{ij}^{(1)}, k \rangle = 0 \quad (k \neq i, j)$$

The application of the antisymmetrizer $\mathcal{A}$ in the final χ_1 then put in these exclusion effects.^{8,62} Since the initial "irreducible" $u_{ij}^{(1)}$

in this approach satisfied the first-order equations of actual non-degenerate two-electron states except for the V_i of the larger "sea", they were adapted to semi-empirical calculations.

On the other hand, for strictly non-empirical calculations, one may apply $\mathcal{A}$ beforehand and get the $\mathcal{B}(ij)$ -type equations (70) directly, without finding the "irreducible pairs" first.^{9b} The action of Q (the $k \neq i, j$ part) in Eq. (70) is equivalent to that of $\mathcal{A}$, and Eq. (70) has a solution for any $\mathcal{B}(ij)$ whether it is degenerate with any other $\mathcal{B}(kl)$ of ϕ_0 or not. Equations (70) and the corresponding ones "to all orders", Eqs. (100), are the easiest to deal with since they avoid the necessity for finding the irreducible pair states first. They are the ones adopted in many-electron theory.^{9b} The relation between irreducible pairs and the $\mathcal{B}(ij)$ -type pairs has been given in detail in Reference 9b and the results of perturbation theory^{8,62} using projection operators have been summarized there. They will not be repeated here.

With Eqs. (70) or (100), the distinct pairs are easily found. For example, in Ne $2p^6$ instead of ^3P , ^1D and ^1S $2p^2$, the three unique pairs can be taken as $(p_x\alpha p_y\beta)$, $(p_x\alpha p_x\beta)$ and $(p_x\alpha p_y\alpha)$. Other pairs differ from these only by changes of axes or by spin permutations. Therefore, one needs to obtain the $\hat{u}_{ij}$'s of these unique pairs only.

The symmetry arguments given above apply to χ_s as well as to χ_1 . The properties of χ_s , even in more complicated cases, e.g. when ϕ_0 is a multi-detor non-closed shell function, can always be found by solving Eq. (64) for the χ_1 by operator techniques^{8,62} and then taking the same *form* for χ_s as this χ_1 .

The symmetry properties of χ_s can also be studied directly, without looking at χ_1 first.

Brickstock and Pople⁸¹ give the *necessary conditions* that the spatial part of a wave function must satisfy if it is to be an eigenfunction of S^2 and S_z .

Consider, for example, a closed shell singlet such as the Be ($1s^2 2s^2 ^1S$). Let the spatial coefficient of the spin function

$$\alpha(1)\alpha(3)\beta(2)\beta(4)$$

in the total w.f. be

$$\Phi(\mathbf{r}_1, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_4) \quad (107)$$

then the conditions given by Brickstock and Pople reduce to

$$\begin{aligned}\Phi(\mathbf{r}_1, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_4) &= -\Phi(\mathbf{r}_3, \mathbf{r}_1; \mathbf{r}_2, \mathbf{r}_4) \\ &= -\Phi(\mathbf{r}_1, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_4)\end{aligned}\quad (108)$$

and to

$$\begin{aligned}\{2\Phi(\mathbf{r}_1, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_4) - \Phi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1, \mathbf{r}_4) \\ - \Phi(\mathbf{r}_4, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_1) - \Phi(\mathbf{r}_1, \mathbf{r}_2; \mathbf{r}_3, \mathbf{r}_4) - \Phi(\mathbf{r}_1, \mathbf{r}_4; \mathbf{r}_2, \mathbf{r}_3)\} = 0\end{aligned}\quad (109)$$

These conditions have been applied by the writer and D. Fu-Tai Tuan to χ_s directly as a check of previous results.^{8, 62} In Be it is confirmed that

$$\begin{aligned}S^2\mathcal{A}(12\hat{u}_{34}) &= S_z\mathcal{A}(12\hat{u}_{34}) = 0 \\ S^2\mathcal{A}(\hat{u}_{12}34) &= S_z\mathcal{A}(\hat{u}_{12}34) = 0\end{aligned}\quad (110)$$

and that only the *combination* of all intershell pairs is a singlet

$$S^2\mathcal{A}(13\hat{u}_{24} + 14\hat{u}_{23} + \hat{u}_{14}23 + \hat{u}_{13}24) = 0 \quad (111)$$

All terms of χ_s individually are $L = 0$ eigenfunctions of L^2 and L_z in Be.

Levine, Geller and Taylor⁶⁴ have obtained by more powerful techniques the *necessary and sufficient* conditions for a wave function to be an eigenfunction of S^2 and S_z .^{*} They find that if

$$S^2\chi_s = 0 \quad (112)$$

then

$$S^2\chi'_s = 0 \quad (113)$$

where χ'_s , Eq. (77), includes the unlinked clusters.

For Be their conditions are

$$\Phi(\mathbf{r}_1, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_4) - \Phi(\mathbf{r}_2, \mathbf{r}_4; \mathbf{r}_1, \mathbf{r}_3) = 0 \quad (114)$$

$$\Phi(\mathbf{r}_1, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_4) - \Phi(\mathbf{r}_2, \mathbf{r}_3; \mathbf{r}_1, \mathbf{r}_4) - \Phi(\mathbf{r}_4, \mathbf{r}_3; \mathbf{r}_2, \mathbf{r}_1) = 0$$

in addition to Eqs. (108).

Writing, e.g.,

$$u_{12}(1,2) = \mathcal{B}\{v_{12}(\mathbf{r}_1, \mathbf{r}_2)\alpha_1\beta_2\} \quad (115)$$

* We are indebted to these authors for making their results available prior to publication and to H. S. Taylor for discussions.

and applying the above conditions to Eq. (111), they find⁶⁴ that for parallel spin pairs

$$v_{ij}(\mathbf{r}_i, \mathbf{r}_j) = -v_{ij}(\mathbf{r}_j, \mathbf{r}_i) \equiv v_{ij}^{\mathcal{A}} \quad (116)$$

and for opposite ($\uparrow\downarrow$) spin pairs

$$v_{kl} = v_{kl}^{\mathcal{A}} + v_{kl}^S \quad (117)$$

where $v_{kl}^{\mathcal{A}}$ refers to antisymmetric and v_{kl}^S to symmetric functions with respect to the interchange of $\mathbf{r}_i$ and $\mathbf{r}_j$, and

$$\begin{aligned} v_{13}^{\mathcal{A}} &= v_{24}^{\mathcal{A}} = v_{14}^{\mathcal{A}} = v_{23}^{\mathcal{A}} \\ v_{14}^S &= v_{23}^S \end{aligned} \quad (118)$$

Thus, there are only two independent pair functions for the intershell part of Be. This confirms the conclusions arrived at from χ_1 ,^{8,62} because $v_{ij}^{\mathcal{A}}$ corresponds to the $^3S(1s2s)$ pair mentioned above and v_{ij}^S to $^1S(1s2s)$. In the $\tilde{\epsilon}'_{ij}$ sum, Eq. (85), *any two linearly independent combinations* of these pairs could be varied separately. Of the choices available, the $\hat{u}_{13}$ and $\hat{u}_{14}$ pairs (linear combinations of ^3S , ^1S pairs⁶²) corresponding to $(1s_\alpha 2s_\alpha)$ and $(1s_\alpha 2s_\beta)$ are the most convenient since they do not necessitate finding the irreducible pair states first. They are the ones used in Eqs. (69), (77) and (86). Once the distinct $\hat{u}_{ij}$'s are determined and the equivalent ones set equal to these, χ'_s should automatically come out to have the proper symmetry. Similarly, the L^2 properties of χ'_s may be examined directly. Again, however, the form of χ_1 above indicates that χ_s is also an eigenfunction of L^2 , once the distinct $\hat{u}_{ij}$'s have been found as in Ne above and independently obtained.

Brickstock and Pople⁸² made a model calculation on Ne by examining the correlations of eight ($2s^2 2p^6$) electrons on the surface of a sphere. They took a trial function of the form⁸¹

$$\tilde{\psi} = \phi_0 F \quad (119a)$$

where

$$F = 1 + \sum_{i>j}^8 \lambda_{ij} f(\mathbf{r}_i, \mathbf{r}_j) \quad (119b)$$

is a "correlation factor".¹

They used Eqs. (108) and (109) and found that $\tilde{\psi}$ is a singlet if all the variational parameters λ_{ij} and the functions $f(\mathbf{r}_i, \mathbf{r}_j)$ are

the same [e.g. the ones for $(p_x \alpha p_y \beta)$ and for $(p_x \alpha p_x \beta)$ have to be the same]. This requirement differs from the one found for χ_s where the $\hat{u}_{ij}$'s of $(p_x \alpha p_y \beta)$ and $(p_x \alpha p_x \beta)$ had to be independent. Note, however, that the form of Eq. (119) is very different from that for χ_s , Eq. (76). In Eq. (119b), $\mathcal{A}$ applies only *within* ϕ_0 and does not apply to the F part.* This makes the form very restrictive and puts on the extra conditions between pair correlations through Eq. (109).

The conclusions of this section are:

(a) χ'_s , Eq. (77), has the same symmetry as ϕ_0 . Both it and the energy, Eqs. (85) and (86), contain a $\hat{u}_{ij}$ for every spin-orbital product $\mathcal{B}(ij)$ formed from the k 's in ϕ_0 .

(b) The number of distinct pairs, $\hat{u}_{ij}$, to be determined are usually found by inspection. Their number is of the order of N . Many of the pairs differ from one another only in their spatial orientation or by spin permutations. In doubtful cases, the distinct pairs can be found by reducing^{8,62} Eq. (64) into pairs or by using equations^{64,81} similar to Eqs. (128) and (114).

This discussion applies to molecules starting with ϕ_0 in the SCF MO description. Then, even for large saturated molecules, there will be a $\hat{u}_{ij}$ for every *molecular orbital pair* $\mathcal{B}(ij)$. However, the theory will be transformed in Section XXVII below into the localized orbitals description. Then the MO $\hat{u}_{ij}$'s will be related to localized correlation functions $\hat{\mu}_{vp}$.

The many-electron theory^{8,9} described in Sections XVI, XVII and XXII now allows atoms and molecules to be built up step by step with a few pair functions. The next three sections will apply the results of the many-electron theory to the first row atoms, to small molecules, and to π -electron systems. Semi-empirical implications of the theory for these cases will also be discussed.

XXIV. ATOMS

We now illustrate the use of the many-electron theory in building up the first row atoms, their ions and lowest excited states step by step. This requires only eleven pair functions for the entire

* The short-hand notation $\phi_0(\hat{u}_{ij}/ij)$ used in Eq. 3. of Reference 10 for the Eq. 20 of this article is erroneous. In our equations $\mathcal{A}$ applies to the $\hat{u}_{ij}$'s as well.

first row and these are used in such a way that some pairs are transferred from system to system and used over and over again.

Both in simplifying non-empirical calculations and for semi-empirical calculation⁶² purposes we wish to know, for example, in just what way the core of a Li atom differs from the free Li^+ ion or from the core of Li_2 .^{*} The H.F. part of this question has been well studied;⁸³ e.g. the core orbitals are known to differ little whether the H.F. method is applied to Na^+ or Na. We shall be concerned here with the correlation part.

Starting with the He isoelectronic series, we give the new pair functions needed as electrons are added one at a time until we reach Ne. As each electron is added not only do new $\hat{u}_{ij}$'s appear, but the old ones are modified.

$(1s^2) \ ^1S$; He, Li^+ , Be^{2+} , . . . , Ne^{8+} : $1s^2$ is a "tight pair" with strictly "dynamical" correlation for which the r_{12} -coordinate method¹ is most appropriate. Take, for example, the Hylleraas⁷⁴ six-term wave function with independent variables $s = r_1 + r_2$, $t = r_2 - r_1$, and $u = r_{12}$. This must now be rewritten as $\mathcal{B}(12) + u_{12}^0$ using Eqs. (104)–(106). The u_{12}^0 would ordinarily be made orthogonal to the H.F. $1s$ orbitals to remove the $\hat{f}_i$, but the $\hat{f}_i$ were calculated above [see after Eq. (92)] and found to give *ca.* 0.0025 ev for He. This effect can therefore be neglected.

$(1s^2 2s) \ ^2S$; Li, Be^+ , B^{2+} , . . . , Ne^{7+} : The same u_{12} is used as in Li^+ , Be^{2+} , etc. The u_{12} in Li, Be^+ , etc. differs from that of the previous series only in the modified V_i , the H.F. "medium" potential and the exclusion effect³ of the $2s$ electron [see Eqs. (81), (86) and (87)]. The u_{12} should be very insensitive to a slight

* Bacher and Goudsmit⁸⁴ used perturbation theory starting with bare nuclei orbitals taken as the ϕ_0 to relate first row atoms to two-electron states semi-empirically. This approach fails in discriminating between small many-electron effects like R' of Eq. (82) and more significant ones resulting from the strong "orbital polarization" of hydrogen-like orbitals (poor charge distribution to start with) and "exclusion effects", Eq. (87). Horák [to be published] uses an improved form of this type of procedure. He still takes the bare nuclei orbitals as the unperturbed ϕ_0 and considers χ_1 and E_2 . However, he calculates the "orbital-polarization effects" (single virtual excitations) explicitly, treating only the double excitations empirically.

change in V_i , because even with a change in the nuclear charge, e.g. in going from He to Li^+ , the $(1s)^2$ correlation is affected by only 0.04 ev^1 and from Li^+ to Be^{2+} by 0.012 ev^1 (Table III). The $2s$ exclusion effect on u_{12} was estimated crudely³ as 0.004 ev in Li (Table III). These changes from say Li^+ to Li being very small one need not vary the parameters of u_{12} again to minimize Eq. (86) for the Li series.⁶² The u_{12} 's from the Li^+ series can be taken over directly and just made orthogonal to $2s$.

Two new pairs, $\hat{u}_{13}$ for $(1s_\alpha 2s_\alpha)$ and $\hat{u}_{23}$ for $(1s_\beta 2s_\alpha)$, are needed when the third electron is added. The variation method is not necessary for these pair functions. Intershell correlations being an order of magnitude* smaller than intrashell ones, they are well approximated by perturbation theory, Eq. (70).

When the two electrons differ in their principal quantum numbers, approximate solutions of Eq. (70) are given by "core-polarization" methods.[†] These methods have been critically examined and a more complete theory which includes penetration effects, etc. given.³

The outer electron (r_3) in Li is less tightly bound and therefore it moves more slowly than an inner electron (r_2). In such a case, the "adiabatic approximation" can be used. The outer electron is considered to be instantaneously at rest and the energy of the core is determined for various fixed values of $\mathbf{r}_3$. This energy depends on $\mathbf{r}_3$ parametrically and in turn acts as a potential energy ["core polarization" potential $V_p(\mathbf{r}_3)$] for the motion of the outer electron $\mathbf{r}_3$. The resulting wave function is

$$\psi_{23}(\mathbf{x}_2, \mathbf{x}_3) = \mathcal{B}\{v_c(\mathbf{r}_2; \mathbf{r}_3)v_o(\mathbf{r}_3)(\beta_2\alpha_3) \quad (120)$$

$v_c(\mathbf{r}_2; \mathbf{r}_3)$ describes the "core" orbital of $\mathbf{r}_2$ and is parametrically dependent on $\mathbf{r}_3$; $v_o(\mathbf{r}_3)$ is the outer electron orbital determined by the H.F. potential of the "core" in addition to the "core-polarization" potential, $V_p(\mathbf{r}_3)$. Again Eq. (120) includes the H.F. part $\mathcal{B}(23)$ so it must be written in the form of Eq. (104) using Eqs. (105) and (106) and then Eq. (71).

* Clementi's⁶⁷ correlation seems too large for $Z = 8, 9$ and 10 . Vincent McKoy pointed out that these values seem to increase as Z^4 . This suggests that relativistic effects which do go as Z^4 may not have been adequately separated.

† For a complete list of references see Reference 3.

TABLE III. Correlation Effects in Li and Li₂

Core polarization energy, ^{a,b} E_p	
Li atom $\left\{ \begin{array}{l} (a) \text{ H.F. SCF } (2s) \\ (b) \text{ OAO } (2s^0) \end{array} \right.$	 -0.1018 ev -0.1066 ev
“Penetration” effects ^c	<0.03 ev
Li ₂ molecule $\left\{ \begin{array}{l} (a') \text{ SCF MO } 2\sigma_g \\ (b') \text{ OMO } (2\sigma_g)^0 \end{array} \right.$	 -0.2473 ev -0.2520 ev
Contribution of E_p to the binding energy (D_e) of Li ₂	
(a') $-2 \times (a)$	-0.044 ev
(b') $-2 \times (b)$	-0.039 ev
D_e of Li ₂ ^d	1.04 ev
Exclusion effect of 2s on Li ⁺ correlation energy ^e	
Change of $(1s^2) E_{\text{corr.}}^e$ from He to Li ⁺	≈0.004 ev
Change of $(1s^2) E_{\text{corr.}}^e$ from Li ⁺ to Be ²⁺	0.040 ev
Core-core dispersion attraction in Li ₂	0.012 ev
	<0.001 ev

^a See text, Section XXIV.

^b Reference 4.

^c Reference 3.

^d Varshni, Y. P., *Rev. Mod. Phys.* **29**, 664 (1957).

^e Reference 1.

The first approximation to Eq. (120) replaces $v_o(\mathbf{r}_3)$ by the H.F. orbital 3. The correlation energy* ϵ_{23} then becomes simply the expectation value of $3(\mathbf{x}_3)$ over $V_p(\mathbf{r}_3)$:

$$\epsilon_{23} = \langle 3, V_p 3 \rangle \quad (121)$$

The $\mathcal{B}(13)$ pair is similar but also includes an exchange term in V_p .

Callaway⁸⁵ obtained numerical values of V_p for Li⁺, Na⁺ and K⁺ in the dipole approximation and used them for the corresponding metals. The same V_p has been applied⁴ to Li and Li₂ and the “penetration” effects left out by Callaway estimated^{3,4} (Table III). Table III also shows the insensitivity of $(\epsilon_{13} + \epsilon_{23})$

* Note that “core-polarization” refers here to the entire correlation effect, polarization by outer electron instantaneously at rest. This should not be confused by the “orbital-average polarization,”^{3,16} i.e. by the spherical potential of the entire 2s orbital which vanishes if complete H.F. is carried out on Li.

to the crudeness of the outer orbital used. The expectation value, Eq. (121), calculated with just a Slater $2s^0$ orbital orthogonal to the core (OAO) differs from the one calculated with the H.F. $2s$ orbital by only 0.005 ev.

$(1s^2 2s^2) {}^1S$; Be, B^+ , C^{2+} , . . . , Ne^{6+} : Again the $\hat{u}_{12} (1s^2)$ can be taken over directly from the Be^+ , . . . , series; there is no new exclusion effect and the V_i change is insignificant.

The intershell correlation is

$$\varepsilon_{13} + \varepsilon_{23} + \varepsilon_{24} + \varepsilon_{14} = 2(\varepsilon_{13} + \varepsilon_{23}) \quad (122)$$

Being insensitive to how accurate the H.F. orbitals are (Table III) and to V_i , the value of this correlation can be taken simply as twice that in the Be^+ , B^{2+} , . . . , series.

The main part of $\hat{u}_{34}$, the correlation in the $2s^2$ shell, is

$$\hat{u}_{34} \cong \gamma(2p)^2 = \gamma\{\det(p_1\beta p_{-1}\alpha) + \det(p_0\alpha p_0\beta) - \det(p_1\alpha p_{-1}\beta)\} \quad (123)$$

owing to near-degeneracy.^{34, 65} γ is the variational parameter to be determined by minimizing ε'_{34} , Eq. (86).

In Watson's⁶⁵ 37 configuration C.I., the $1s^2(2p)^2$ configuration contributed about 1.2 ev (corrected for unlinked clusters).^{9b} Note that in the many-electron theory, even when C.I. is needed, it is done only on one pair at a time, requiring very few matrix elements and a very small secular equation compared with the full C.I. treatment applied to the entire ψ and H .

The $\hat{u}_{34}$, Eq. (123), gives

$$\varepsilon_{34} \propto Z \quad (124)$$

for the Be, B^+ , C^{2+} , . . . , series.³⁴

$(1s^2 2s^2 2p_z) {}^2P$; B, C^+ , N^{2+} , . . . , Ne^{5+} : The $1s^2$ pair $\hat{u}_{12}$ from the B^+ series must now be orthogonalized [Eq. (71)] to $(5) \equiv 2p_0\alpha$. "Exclusion effects" on such "dynamical" $\hat{u}_{ij}$ will, in general, be small.

The $2p_z$ exclusion on $\hat{u}_{34}$, Eq. (123), is very important, however.^{9a} It eliminates the $\det(p_0\alpha p_0\beta)$ part of Eq. (123) giving

$$\hat{u}_{34} \simeq \gamma'\{\det(p_1\beta p_{-1}\alpha) - \det(p_1\alpha p_{-1}\beta)\} \quad (125)$$

This effect increases as more $2p$ electrons are added (see C, N, . . . , Ne below). For the isoelectronic series $(1s^2 2s^2 2p_z)$ ϵ_{34} may still be linear in Z , but in going from B^+ to B, Eq. (123) to (125), $|\epsilon_{34}|$ is reduced from 1.2 ev. to *ca.* 0.82 ev.* The exclusion effect localizes $\hat{u}_{34}$, Eq. (125), to the plane perpendicular to $2p_z$. This makes the $2s^2 2p_z$ three-electron correlation small. The fluctuation potential between a $2s$ and a $2p_z$ electron is small just where $\hat{u}_{34}$ is large (see Figs. 1 and 2 in Reference 9a).

The new $(1s\alpha 2p_z\alpha)$ and $(1s\beta 2p_z\alpha)$ pairs, $\hat{u}_{15}$, $\hat{u}_{25}$, are simply obtained by taking the expectation value of $H.F. (2p_z)$ over the same $1s^2$ core-polarization potential that was used in B^{2+} or B^+ . The result could be improved, however, by making the corresponding u_{ij} 's from Eq. (120) orthogonal to $2p_z$.

The $2s2p$ pairs $\hat{u}_{35}$, $\hat{u}_{45}$ may be obtained by the C.I. or the r_{12} method or other methods used in connection with Eq. (86).

$(1s^2 2s^2 2p^2) {}^3P, {}^1D, {}^1S$; C, N^+ , O^{2+} , F^{3+} , Ne^{4+} : Most pairs within these ions are similar to those discussed for the previous series. The non-dynamical part of u_{34} now reduces to

$$\hat{u}_{34} \cong \gamma'' \{ \det (p_0 \alpha p_0 \beta) \} \quad (126)$$

for the ${}^3P$ case, $|\epsilon_{34}|$ dropping to *ca.* 0.5 ev.⁸⁶ Whether dynamical effects now become important in $\hat{u}_{34}$ is uncertain (see below).

The empirical $\hat{u}_{56}, (p_1 \alpha p_{-1} \alpha)$ correlation in ${}^3P$ seems to be roughly 0.05 ev.⁶⁷ Any of the methods discussed below for Ne may be used for the $2p^2$ pairs in ${}^3P$, ${}^1D$ or ${}^1S$.

$(1s^2 2s^2 2p^3) {}^4S, {}^2D, {}^2P$; N, O^+ , F^{2+} , Ne^{3+} : The pairs are similar to those in the previous series. The empirical $(2p)^3$ correlation⁶⁷ is *ca.*

$$\epsilon_{56} + \epsilon_{67} + \epsilon_{75} \cong 0.1 \text{ ev} \quad (127)$$

in nitrogen (${}^4S$) (see Fig. 1).⁶⁷

The exclusion effect of these $2p$ electrons reduces the non-dynamical $\hat{u}_{34}$ of the previous series to zero in ${}^4S$ here. This part

* Glembotskii, Kibartas and Yutsis⁸⁶ did "extended H.F." on the two configurations too, but the results differ little from H.F. on $\phi_0 (1s^2 2s^2 2p_z)$ alone followed by C.I. In beryllium three-configuration "extended H.F." differs from H.F. + C.I. by *ca.* 0.03 ev.

of $\hat{u}_{34}$ and ε_{34} remains zero in O, F and Ne, since the $2p_x$, $2p_y$, $2p_z$ orbitals are already occupied in all these atoms.

In the Be series, ε_{34} was found to be linearly dependent on Z .³⁴ On the other hand, we showed above that in going from Be to Ne, as more and more electrons are added this linear dependence of

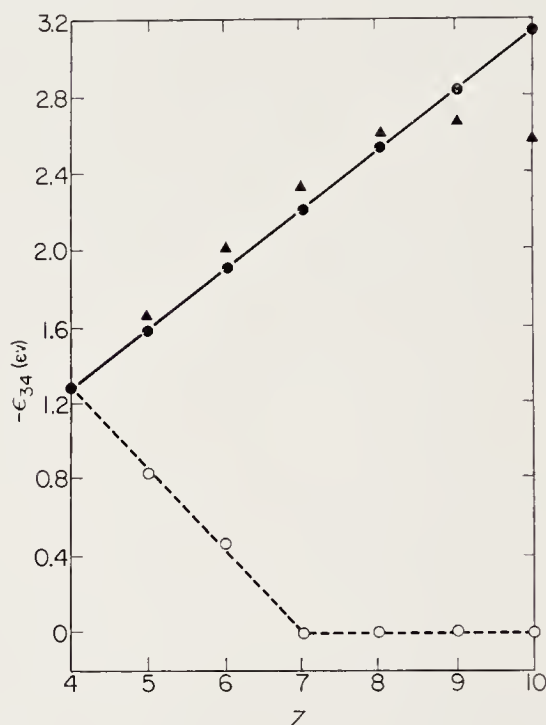


Fig. 4. Exclusion effect of $2p$ electrons on the correlation energy ε_{34} of the $(2s^2)$ pair (see text, Section XXIV) ▲: Empirical $(2s^2)$ correlation energies in atoms Be, B, C, N, F and Ne (based on E. Clementi's empirical data⁶⁷). —●—: Energy lowering in the ions Be, B^+ , C^{2+} , . . . , Ne^{6+} due to $2s^2-2p^2$ mixing (near-degeneracy) (Linderberg and Shull³⁴). —○—: Near degeneracy part of ε_{34} in the atoms Be through Ne. The $2p^2$ mixing to $2s^2$ is diminished by the exclusion effect of electrons already occupying $2p$ orbitals.

ε_{34} can no longer be expected. Recent empirical results, however,⁶⁷ still show an increase of correlation energies with Z in these atoms. This discrepancy means that either the empirical results need to be re-examined, perhaps in the estimates of the relativistic effects, or else the dynamical part of $\hat{u}_{34}$, which was small in Be, is gaining importance as Ne is approached (see Fig. 4). This question is being investigated by V. McKoy in the writer's laboratory.

($1s^2 2s^2 2p^6$) ^1S ; F^- , Ne , Na^+ , . . .: The inner shells and core polarization pairs may be taken over from the previous series. For $(2p)^6$, three new pair functions corresponding to $(p_x \alpha p_x \beta)$, $(p_x \alpha p_y \beta)$ and $(p_x \alpha p_y \alpha)$ are needed. These may be obtained by the r_{12} -method or C.I. using Eqs. (86), but an "open shell" or "different orbitals for different spins"¹ method seems particularly suitable. Calculations on Ne and other first row atoms along the lines indicated are being made in the writer's laboratory.

The above discussion shows that with eleven pair functions, six of which are significant, all the first row atoms and ions can be built up.^{3,8,9} Many of the pairs are used over and over again and new integrations are performed only for additional exclusion effects.

From the u_{ij} 's, $\hat{f}_i$ and R' of Eq. (82) can be calculated too to estimate the errors due to their neglect in the theory. Note that the r_{12} -coordinate method is suitable in only a few pairs. One would not necessarily obtain better results using it on all pairs. With only a few r_{ij} in χ'_s , the integrals needed in R' are simpler⁹ than with r_{ij} 's in all $\hat{u}_{ij}$'s.^{19,25,48b}

It should be of interest to check R' , e.g. in Ne , though this seems no longer crucial since the additivity predicted by the theory, Eq. (85), has now been empirically confirmed.⁶⁷

Equation (85) and the above discussion of specific pairs give some justification for the semi-empirical theories used for atomic spectra. Cores are little affected by outer electrons and intershell correlation is simply included through the empirical core potential. Equation (85) has just *the same form* as the H.F. part of the energy alone [Eqs. (11) and (13)]. Thus, empirical F and G parameters¹³ include correlation.

XXV. SMALL MOLECULES

The procedures outlined above for atoms also apply to small molecules, e.g. LiH , Li_2 , N_2 , HF , F_2 , etc. For these, the theory starts with H.F. SCF MO's;²⁸ the $\hat{u}_{ij}$'s refer to MO pairs. The inner shells, however, can be taken directly from free atoms after an equivalent orbital transformation has been performed on say the $(1\sigma_g)^2(1\sigma_u)^2$ part of Li_2 as shown in Section XXVII below. The "exclusion" and "medium" effects on the innermost shells

are again small; e.g. the Li_2 cores are expected to differ from the Li core or Li^+ by less than 0.01 eV (Table IV; see changes from Li^+ to Li core). This means changes in the inner core correlation energies can safely be neglected in comparing atoms and molecules to calculate binding energies.

Once H.F. is available, E_{corr} , and hence binding energies are easily estimated by applying Eq. (85) to the molecule and to the dissociated atoms. Assuming $\varepsilon_{ij} \approx 1$ to 1.5 eV for a doubly occupied pair and neglecting the rest, for the formation of a diatomic molecule from atoms A and B



$$\Delta E_{\text{corr.}} \cong \langle \varepsilon_{ij} \rangle \Delta n \quad (127)$$

where $\langle \varepsilon_{ij} \rangle$ is an empirical average pair correlation energy and Δn is the net increase in the number of doubly occupied pairs upon molecule formation. On this basis, for example,

$$\begin{aligned} 2\text{N}(^4\text{S}) = \text{N}_2; \quad \Delta E_{\text{corr.}} &\approx -3.9 \mp 0.6 \text{ eV} \\ 2\text{F}(^2\text{P}) = \text{F}_2; \quad \Delta E_{\text{corr.}} &\approx -1.3 \mp 0.2 \text{ eV} \end{aligned} \quad (128)$$

Stanton⁸⁷ has discussed such a semi-empiricism.

The separation of valence electrons in Eq. (85) and the lack of the “nightmare of inner shells”⁸⁸ in minimizing just the outer $\tilde{\varepsilon}'_{ij}$'s, Eq. (86), allow one to consider now heavier systems like Na_2 and BaO . The binding energies and other properties of even such molecules may now be calculated just from the minimization of the $\tilde{\varepsilon}'_{ij}$'s of the valence electrons combined with the H.F. part of their energy. The trial functions would be kept orthogonal to the atomic H.F. core orbitals.

XXVI. π -ELECTRON SYSTEMS

Many-electron theory justifies the “ π -electron approximation”^{11,12} mentioned in Section III. Equation (85) separates the Σ and Π shells. Writing out the H.F. part, Eqs. (13), and combining it with the correlation part, one gets from Eq. (85)

$$E_s'' = \sum_{i=1}^N \langle i, h_i^o i \rangle + \sum_{i>j}^N (J_{ij} - K_{ij}'' + \tilde{\varepsilon}'_{ij}) \quad (128)$$

This again is of the same *form* as $E_{\text{H.F.}}$ alone. The exact equation (60) was also of this form. Note, however, that to justify the separate treatment of shells the $\tilde{\epsilon}_{ij}$'s must be decoupled as in Eqs. (128) and (85). In the exact E , Eq. (60), on the other hand, the pair energies and the $\hat{U}'_{ij}$'s could in principle depend very strongly on each other and on $\hat{f}_i$ and $\hat{U}_{ijk}$, etc. [compare Eqs. (20) and (76) or (77)].

The part of R coupling the Σ - and Π -electrons in Eq. (82) will be small because of the reasons given in Section XVIII, particularly the localization of these separate shells. The many-electron terms R' between π -electrons themselves, on the other hand, should be small mainly on account of Eq. (87). It would be interesting to check the magnitude of R' , e.g. in benzene.

As in atomic spectra, the form of Eq. (128) shows why the semi-empirical parameters of π -electron theory¹² tend to include correlation. "Zero differential overlap" allows the J_{ij} integrals in the H.F. part of Eq. (128) to be broken down into one- and two-center Coulomb integrals. The large difference between the non- and semi-empirical values of these is accounted for by introducing^{14,15} correlation into $(2p_z)^2$. This is justified because the "zero differential overlap" can equally well be made in the $\tilde{\epsilon}_{ij}$'s, reducing them to one- and two-center Coulomb correlation energies.

For π -electron spectra, one may start at least formally with H.F. based on the "average energy of a configuration",³³ with symmetry and equivalence restrictions (see Section VI). As results on atoms also indicate, the $\tilde{\epsilon}_{ij}$'s of Σ cores as well as core-polarization potentials will not be much affected by the valence electrons, so that one deals with just the Π part of Eq. (128).

Equation (128) can be written as^{9b}

$$E_s'' = E_\Sigma + E_\Pi + \epsilon_{\sigma\pi} \quad (129)$$

$$E_\Sigma = \sum_{i \geq 1}^{n_\sigma} \langle i, h_i^o i \rangle + \sum_{i > j \geq 1}^{n_\sigma} (\bar{J}_{ij} + \tilde{\epsilon}'_{ij}) \quad (130)$$

$$E_\Pi = \sum_{k > n_\sigma}^{n_\pi} \langle k, h_k^o k \rangle + \sum_{l > k > n_\sigma}^{n_\pi} (\bar{J}_{kl} + \tilde{\epsilon}'_{kl}) \quad (131)$$

$$\epsilon_{\sigma\pi} = \sum_{i \geq 1}^{n_\sigma} \sum_{k > n_\sigma}^{n_\pi} \tilde{\epsilon}'_{ik} \quad (132)$$

n_σ and n_π are the numbers of σ - and π -electrons. E_Σ is the core energy including correlation; it is assumed to be the same regardless of which π -orbitals are occupied. E_Π is the Π -shell energy in the field of a static (H.F.) core. $\varepsilon_{\sigma\pi}$ is the intershell correlation. It can be added either as a small correction by perturbation theory or evaluated in the adiabatic approximation,³ Eq. (120). Then

$$\varepsilon_{\sigma\pi} \cong \sum_{k > n_\sigma}^{n_\pi} \langle k, V_p(\mathbf{x}_k) k \rangle \quad (133)$$

where the k 's are SCF π -MO's, and V_p is the core-polarization potential which is determined only by the core. V_p is the same regardless of which k it is acting upon.

A formal justification of the simple Hückel theory has been given by Simpson.⁸⁹

Using Eqs. (8), (16) and (86), E_Π or Eq. (131), e.g. for ethylene, may be written as

$$E_\Pi \leq \tilde{E}_\Pi = E_\Pi^{\text{H.F.}} + \frac{2\langle \mathcal{B}(kl), m_{kl} \hat{u}_{kl} \rangle + \langle \hat{u}_{kl}, (e_k + e_l + m_{kl}) \hat{u}_{kl} \rangle}{1 + \langle \hat{u}_{kl}, \hat{u}_{kl} \rangle} \quad (134)$$

where k, l are the two π -electrons. But in $(e_k + e_l + m_{kl})$ we have [see Eqs. (12) and (17)]:

$$V_k + V_l - \tilde{S}_k - \tilde{S}_l = V_{\text{core}}(\mathbf{x}_k) + V_{\text{core}}(\mathbf{x}_l) \quad (135)$$

i.e. the "core" parts of H.F. potentials V_i . Then writing^{9b}

$$\hat{\psi}_{kl} \equiv \mathcal{B}(kl) + \hat{u}_{kl}$$

we have

$$E_\Pi \leq \tilde{E}_\Pi = \frac{\langle \hat{\psi}_{kl}, (\mathcal{H}_k^{\text{core}} + \mathcal{H}_l^{\text{core}} + r_{kl}^{-1}) \hat{\psi}_{kl} \rangle}{\langle \hat{\psi}_{kl}, \hat{\psi}_{kl} \rangle} \quad (136)$$

This is the π -part which has to be minimized separately subject to $\langle \hat{u}_{kl}, \hat{u}_{kl} \rangle = 0$ to obtain the $\hat{\psi}_{kl}$. Note that

$$\mathcal{H}_k^{\text{core}} + \mathcal{H}_l^{\text{core}} + \frac{1}{r_{kl}} = \mathcal{H}_\Pi \quad (137)$$

is just the " π -electron Hamiltonian" which was postulated on an intuitive basis before.^{11,12} The V_p "core-polarization potentials" in Eq. (133) can be incorporated into the $\mathcal{H}_i^{\text{core}}$, too.³

With more than two π -electrons

$$E_{\Pi} \leq \frac{\langle \hat{\psi}_{\Pi}, \mathcal{H}_{\Pi} \hat{\psi}_{\Pi} \rangle}{\langle \hat{\psi}_{\Pi}, \hat{\psi}_{\Pi} \rangle} \quad (138)$$

$$\hat{\psi}_{\Pi} = \mathcal{A}\{(n_{\sigma} + 1)(n_{\sigma} + 2) \dots n_{\pi}\} + \chi_{\Pi} \quad (139)$$

$$\mathcal{H}_{\Pi} = \sum_{k > n_{\sigma}}^{n_{\pi}} \mathcal{H}_k^{\text{core}} + \sum_{k > l}^{n_{\pi}} \left(\frac{1}{r_{kl}} \right) \quad (140)$$

χ_{Π} is of the form given in Eq. (77), but it may also include many-electron correlations $\hat{U}_{ijk}$, $\hat{U}_{ijkl}$, . . . , as in the exact χ , Eq. (20), if one is dealing say with a nearly “metallic” dye molecule.

XXVII. LOCALIZATION—BONDS, LONE PAIRS, ION CORES

The theory thus far presented is based on the MO description with $\hat{u}_{ij}$'s for MO pairs even if one is dealing with a large saturated molecule in which electrons are strongly localized. The theory in this form separates the “concentric” shells (inner and outer shells), but for saturated molecules we still have to see how localized bonds and lone pairs come about, why bond energies are quite independent of molecular environment, and what the forces between bonds are. Fortunately, one does not have to start anew with a different theory for such systems. A simple transformation turns the MO-based many-electron theory into the localized description.

This problem too has an orbital and a correlation part. The orbital part was solved by Lennard-Jones,^{35a,37} who showed that in an H.F. SCF MO determinant, ϕ_0 , electrons are already localized with respect to one another (e.g. in CH_4 , H_2O , Ne , . . .) as mentioned in Section VII. This relative distribution of electrons with respect to one another is better described by a unitary “equivalent” or “localized” orbital transformation $\mathbf{t}$ which leaves ϕ_0 unchanged:

$$k = \sum_{v \geq 1}^N t_{kv} \eta_v \quad (141a)$$

$$\eta_v = \sum_k^N \bar{t}_{vk} k \quad (141b)$$

where $k = 1, 2, 3, \dots, N$ are the H.F. SCF MO's with spin in ϕ_0 , η_ν are the new localized spin-orbitals, and $\{\bar{t}_{\nu k}\}$ is the complex conjugate transpose, i.e. adjoint matrix to $\mathbf{t}$.

Note that Eq. (141) actually contains two independent transformations, one for odd k , i.e. α spin-orbitals, and one for even k , i.e. β spin-orbitals.

With

$$\phi_0 = \mathcal{A}(123 \dots k \dots N) = \mathcal{A}(\eta_1 \eta_2 \dots \eta_\nu \dots \eta_N) \quad (142)$$

E_0 and E_1 , Eqs. (11) and (13), remain of the same form:

$$E_0 = \sum_{\nu \geq 1}^N \varepsilon_\nu \quad (143)$$

$$E_1 = - \sum_{\rho > \nu} (J_{\rho\nu} - K''_{\rho\nu}) \quad (144)$$

but Eqs. (12) no longer apply; instead, one has

$$e_\nu \eta_\nu = \sum_{\rho \neq \nu} \gamma_{\nu\rho} \eta_\rho; \quad e_\nu = h_\nu^o + V_\nu - \varepsilon_\nu \quad (145)$$

$\gamma_{\nu\rho}$ are the off-diagonal H.F. orbital energies and ε_ν is a diagonal orbital energy. h_ν^o and V_ν are the same as before [Eqs. (4a) and (8) with $\mathbf{x}_\nu$ replacing $\mathbf{x}_i$].*

In CH_4 , the equivalent C—H orbitals^{37,38} are determined by symmetry. In other molecules with less symmetry, e.g. H_2O , C_2H_6 , etc., $\mathbf{t}$ may be determined so as to minimize the magnitude of the exchange terms^{39,46} in Eq. (144), or by a similar criterion.⁴⁰

Localized orbitals have been studied extensively by Pople,^{35b} Linnett^{35c} and Hall^{39b}. Very recently, Ruedenberg and Edmiston have developed a procedure for calculating them based on the "minimum exchange" criterion.³⁹

Hall^{39b} correlated the ionization potentials of hydrocarbons, ethane to decane, assuming unchanged localized orbitals and energies ε_ν and $\gamma_{\rho\nu}$.

* That all the operators in h_i^{eff} are invariant under the transformation $\mathbf{t}$ is obvious except perhaps for V_i which depends on the orbitals. V_i , Eq. (8), can be written in terms of the Fock–Dirac density $\rho(\mathbf{x}_i, \mathbf{x}_j)$.¹ The summation in $\rho(\mathbf{x}_i, \mathbf{x}_j)$ covers a set of molecular orbitals which form a basis for certain irreducible representations. This is invariant under any unitary transformation.³⁷

Ionization potentials are not affected much by electron correlation ("Koopman's theorem").¹ For heats of formation and conformational changes, however, correlation is all-important.²

Hurley, Lennard-Jones and Pople²⁰ put correlation into localized groups by the *ad hoc* wave function

$$\mathcal{A}\{\Lambda_A(\rho, \nu) \Lambda_B(\lambda, \tau) \cdot \cdot \cdot\} \quad (146)$$

and the arbitrary condition, Eq. (1). The limitations of this approach^{21,22} were discussed in Section IV after Eq. (1) and elsewhere^{20,3,9b,23,24,25} (see footnote 29 of Reference 9b). Among other limitations Eq. (146) does not allow one to go from localized properties in the ground state to the properties of delocalized electrons in connection with electronic spectra.

Fortunately, a separate theory for localized groups and another one for delocalized electrons are not needed. Both are handled by the same "many-electron theory". One has only to know how χ and E_{corr} transform⁹⁰ under the same $\mathbf{t}$ that transformed ϕ_0 . One can then go back and forth between spectral and localized properties.¹⁰

A. Transformation on the Exact Energy

In terms of the *molecular* MO spin-orbitals i, j , the *exact* energy is given by Eq. (60). To see how correlation energy transforms when the transformation of Eq. (141a) is applied to H.F. MO's, substitute

$$\mathcal{B}(ij) = \sum_{\nu > \rho}^N t_{i\nu} t_{j\rho} \mathcal{B}(\eta_\nu \eta_\rho) \quad (147)$$

into Eq. (60)

$$E_{\text{exact}} = E_{\text{H.F.}} + \sum_{i > j}^N \langle \mathcal{B}(ij), g_{ij} \hat{U}'_{ij} \rangle \quad (60'a)$$

where

$$\langle \hat{U}'_{ij}, k \rangle = 0 \quad (k = 1, 2, 3, \dots, i, j, \dots, N) \quad (60'b)$$

Interchanging the order of summations and noting that the operator is the same for all the electrons, one gets

$$E = E_{\text{H.F.}} + \sum_{\nu > \rho}^N \langle \mathcal{B}(\eta_\nu \eta_\rho), g_{\nu\rho} \hat{\mu}_{\nu\rho} \rangle \quad (148)$$

$$\hat{\mu}_{\nu\rho} = \sum_{i > j}^N \bar{t}_{\nu i} \bar{t}_{\rho j} \hat{U}'_{ij} \quad (149)$$

We still have

$$\langle \hat{\mu}_{vp}, k \rangle = 0 \quad (150)$$

where the k are still the MO spin-orbitals.

$\hat{\mu}_{vp}$ are the correlation w.f.'s between localized spin-orbitals. They too are localized. For a given $\hat{\mu}_{vp}$, if v and ρ differ only in their spin, $\hat{\mu}_{vp}$ is the correlation w.f. of that bond, lone pair or inner shell pair like $(1s)^2$ in Li_2 . If, on the other hand, v and ρ refer to localized orbitals with different spatial parts (intershell correlation), the corresponding $\hat{\mu}_{vp}$ gives the van der Waals attraction *between* the localized orbitals of separate groups.

When the MO pair functions $\hat{U}_{ij}$ are available, say in a C.I. or r_{12} form, etc., Eq. (149) gives the correlations in the localized description immediately. For instance, Eq. (149) could be applied to the H.F. MO + C.I. results of Nesbet³⁸ on the CH_4 molecule thereby extracting from them the C—H bond correlation energy and the “van der Waals attraction” between two different C—H bonds.

Equation (149) proves that $E_{\text{corr.}}$ of a saturated molecule is exactly equal to the sum of the bond, lone-pair and ion-core correlation energies and the intramolecular van der Waals attractions between these groups. This result is as accurate as the Schrödinger equation itself but so far it is purely formal. The exact $\hat{\mu}_{vp}$ that appear in Eq. (148) are related to the exact χ , Eq. (20), in the same way as the $\hat{U}_{ij}$ of Eq. (60) were; they can in principle depend on all the other terms of χ .

The following questions then remain: (i) How can the $\hat{\mu}_{vp}$ be obtained directly (since this may be more convenient than getting the $\hat{u}_{ij}$ first)? (ii) What are the environmental effects implicit in $\hat{\mu}_{vp}$ and the localized correlation energies

$$\varepsilon_{vp} \equiv \langle \mathcal{B}(\eta_v \eta_\rho), g_{vp} \hat{\mu}_{vp} \rangle \quad (151)$$

B. Transformations on the Approximate Energies

The energy expressions given by perturbation theory and the many-electron theory are also of the form Eq. (60').

With the first-order pair function $\hat{u}_{ij}^{(1)}$ satisfying Eq. (70), Eq. (69) gives the energy to the second order as

$$E \cong E_{\text{H.F.}} + E_2 = E_{\text{H.F.}} + \sum_{i>j}^N \langle \mathcal{B}(ij), g_{ij} \hat{u}_{ij}^{(1)} \rangle \quad (152)$$

In the many-electron theory, when each $\tilde{\varepsilon}'_{ij}$, Eq. (86), is minimized so that the pairs "to all orders" satisfy Eqs. (100), $\tilde{\varepsilon}'_{ij}$ reduces to ε_{ij} , Eq. (101); Eq. (85) becomes again

$$E_s'' = E_{\text{H.F.}} + \sum_{i>j}^N \langle \mathcal{B}(ij), g_{ij} \hat{u}_{ij} \rangle \quad (153)$$

Note that Eqs. (60), (152) and (153) all *look* the same. The pair correlation function $\hat{u}_{ij}$ in each is, however, different. Contrary to Eq. (60), which is derived from the exact χ , in Eqs. (152) and (153) the pairs are decoupled and do not implicitly depend on f_i , or on $\hat{U}_{ijk}, \hat{U}_{ijkl}$, etc.

As the forms are the same, the transformations of Eqs. (147) and (149) apply to Eqs. (152) and (153) as well. The resulting equations are similar to Eq. (148) but now contain the first-order $\hat{\mu}_{\rho\nu}^{(1)}$ or the "exact" (all orders) pairs $\hat{\mu}_{\rho\nu}$ of the "many-electron theory". We have

$$E_2 = \sum_{\nu>\rho}^N \langle \mathcal{B}(\eta_\nu \eta_\rho), g_{\nu\rho} \hat{\mu}_{\nu\rho}^{(1)} \rangle \quad (152b)$$

and

$$E_s'' = E_{\text{H.F.}} + \sum_{\nu>\rho}^N \langle \mathcal{B}(\eta_\nu \eta_\rho), g_{\nu\rho} \hat{\mu}_{\nu\rho} \rangle \quad (153b)$$

The distinction between the $\hat{\mu}_{\nu\rho}$ in Eq. (153b) and the $\hat{\mu}_{\nu\rho}$ in Eq. (148) is similar to that between $\hat{u}_{ij}$ and the $\hat{U}_{ij}$ which come from the full exact χ .

C. Transformations on the Variational Energies

Equations (152) and (153) in the previous section hold only for the pair functions which satisfy their respective effective Schrödinger equations (70) or (100a). To obtain the MO pairs $\hat{u}_{ij}$, one needed to minimize variational expressions like Eq. (86). In the same way, Eqs. (152b) and (153b) hold only for the optimum $\hat{\mu}_{\rho\nu}$. To obtain these directly one must have a variational principle for each $\hat{\mu}_{\rho\nu}$.

The utility of the "bond energy" concept shows that it should be easier to obtain the $\hat{\mu}_{\rho\nu}$ for the localized and van der Waals type correlations directly and individually when dealing with a large molecule rather than to obtain the $\hat{u}_{ij}$ first. This is of great

practical importance. To calculate say an S—H bond energy *a priori*, one should not have to obtain the MO's of, say, an entire protein molecule or to carry out a complete H.F. + C.I. calculation on it first.

To see how the $\hat{\mu}_{vp}$ may be calculated directly let us consider first the perturbation theory. The variational form of Eq. (152) was [see Eqs. (63), (64) and (103)]

$$E_{\text{H.F.}} + E_2 \leq E_{\text{H.F.}} + \tilde{E}_2 \quad (154a)$$

$$\tilde{E}_2 = \sum_{i>j}^N \tilde{\varepsilon}_{ij}^{(2)} \quad (154b)$$

$$\varepsilon_{ij}^{(2)} \leq \tilde{\varepsilon}_{ij}^{(2)} \equiv 2\langle \mathcal{B}(ij), g_{ij} \hat{u}_{ij}^{(1)} \rangle + \langle \hat{u}_{ij}^{(1)}, (e_i + e_j) \hat{u}_{ij}^{(1)} \rangle \quad (154c)$$

$$\delta \tilde{\varepsilon}_{ij}^{(2)} = 0; \quad \langle \delta \hat{u}_{ij}^{(1)}, k \rangle = 0; \quad k = (1, 2, 3, \dots, i, j, \dots, N) \quad (154d)$$

The $\hat{u}_{ij}^{(1)}$'s are trial functions for the first-order MO pair functions. They approach the $\hat{u}_{ij}^{(1)}$'s as $\tilde{\varepsilon}_{ij}^{(2)} \rightarrow \varepsilon_{ij}^{(2)}$.

The first sum in E_2 is the same as in Eq. (152); it is transformed by the substitution of Eqs. (147) and (149). The $[(h_i^o + V_i) + (h_j^o + V_j)]$ part of $e_i + e_j$ [see Eqs. (7) and (12) and the footnote on page 388] is the same for all electrons. Hence the inverse of Eq. (149) gives

$$\sum_{i>j}^N \langle \hat{u}_{ij}^{(1)}, (h_i^{\text{eff}} + h_j^{\text{eff}}) \hat{u}_{ij}^{(1)} \rangle = \sum_{v>\rho}^N \langle \hat{\mu}_{vp}^{(1)}, (h_v^{\text{eff}} + h_\rho^{\text{eff}}) \hat{\mu}_{vp}^{(1)} \rangle \quad (155)$$

Note that only the name of the dummy variable in h_i^{eff} has been changed. Otherwise h_i^{eff} and h_v^{eff} are *the same*; they both involve the V_i of the *entire* molecule as given by Eq. (8) with MO's.

The MO orbital energies part $(\varepsilon_i + \varepsilon_j)$ of $e_i + e_j$ is different for each pair; so using the inverse of Eq. (149) *twice*, on the left and on the right, one gets

$$\sum_{i>j}^N \langle \hat{u}_{ij}, (\varepsilon_i + \varepsilon_j) \hat{u}_{ij} \rangle = \sum_{v>\rho}^N \sum_{\sigma>\tau}^N \langle \hat{\mu}_{vp}, \{ \sum_{i>j}^N \bar{t}_{vi} \bar{t}_{\rho j} (\varepsilon_i + \varepsilon_j) t_{i\sigma} t_{j\tau} \} \hat{\mu}_{\sigma\tau} \rangle \quad (156)$$

The superscripts on the u 's and μ 's have been omitted for simplicity.

Finally, Eq. (154) becomes

$$\tilde{E}_2 = \sum_{v>\rho}^N \tilde{\varepsilon}_{vp}^{(2)} + \Delta^{(2)} \quad (157a)$$

$$\tilde{\varepsilon}_{vp}^{(2)} = 2\langle \mathcal{B}(\eta_v \eta_\rho), g_{vp} \tilde{\mu}_{vp}^{(1)} \rangle + \langle \tilde{\mu}_{vp}^{(1)}, (e_v + e_\rho) \tilde{\mu}_{vp}^{(1)} \rangle \quad (157b)$$

$$\Delta^{(2)} = \sum_{\substack{v>\rho \\ v,\rho \neq \sigma,\tau}}^N \sum_{\substack{\sigma>\tau \\ v,\rho \neq \sigma,\tau}}^N (\gamma_{v\sigma} + \gamma_{\rho\tau}) \langle \tilde{\mu}_{vp}^{(1)}, \tilde{\mu}_{\sigma\tau}^{(1)} \rangle \quad (157c)$$

In Eq. (156) we have used

$$\mathbf{t}\bar{\mathbf{t}} = \mathbf{I} \quad (158a)$$

and ^{37b}

$$\mathbf{t}\mathbf{e}\bar{\mathbf{t}} = \boldsymbol{\gamma} \quad (158b)$$

ϵ are the MO orbital energies, and $\boldsymbol{\gamma}$ is the localized orbital energy matrix [see Eqs. (143) and (145)]. In Eq. (157b)

$$\gamma_{vv} = \varepsilon_v \quad (158c)$$

According to the variation-perturbation procedure, one would now minimize each $\tilde{\varepsilon}_{vp}^{(2)}$ with trial functions $\tilde{\mu}_{vp}^{(1)}$ subject to

$$\langle \tilde{\mu}_{vp}^{(1)}, k \rangle = 0 \quad (k = 1, 2, 3, \dots, N) \quad (157d)$$

where the k are still the entire MO's. This procedure and the environmental effects brought in by the k and the entire H.F. ϕ_0 potentials V_v in Eq. (157b) are discussed in the next section.

The coupling terms $\Delta^{(2)}$ are easily estimated. They are much smaller than the $(\sum_{v>\rho} \varepsilon_{vp}^{(2)})$ term so that the variation-perturbation procedure applies (Section XIV). The $\tilde{\mu}_{vp}^{(1)}$ calculated from Eqs. (157b) alone can be used to calculate the $\Delta^{(2)}$ as well.

Hall^{39b} obtained empirical values for the off-diagonal H.F. energies γ_{vp} of the hydrocarbons methane to decane. By applying Eq. (149) to Nesbet's³⁸ H.F. MO + C.I. function for CH_4 a crude estimate of the $\langle \tilde{\mu}_{vp}^{(1)}, \tilde{\mu}_{\sigma\tau}^{(1)} \rangle$ is obtained.⁹¹ With $\gamma_{vv} = -13.75$, $\gamma_{\rho v} = -1.75$ ev, this gives for methane

$$\Delta^{(2)} \cong +0.1 \text{ ev} \quad (158)$$

as compared to

$$\sum_{v>p}^N \tilde{\epsilon}_{vp}^{(2)} \cong -7 \text{ ev}$$

The -7 ev is an empirical estimate for the total correlation energy of CH_4 ; it is *not* Nesbet's³⁸ value, which was 1.95 ev .

Where E_2 is sufficient then, the $\hat{\mu}_{pv}$ can be approximated by $\hat{\mu}_{pv}^{(1)}$ obtained by minimizing Eqs. (157b).

Consider now the *complete upper limits* given to E by wave functions of the form of Eqs. (69a) and (76). The energy, Eq. (65), obtained with χ_1 contains E_3 . Equation (65), written out in detail, is of the *same form* as E_s , Eq. (78), but it contains the $\hat{u}_{ij}^{(1)}$ obtained by the minimization of the smaller portion, Eq. (154c), of $\tilde{\epsilon}_{ij}$. Comparison of Eqs. (65), (154c) and (78) then shows that E_3 includes the third-order corrections to pairs as well as the three-electron terms

$$E_3 = \sum_{i>j}^N \langle \hat{u}_{ij}^{(1)}, m_{ij} \hat{u}_{ij}^{(1)} \rangle + R^{(3)} \quad (159)$$

$R^{(3)}$ is given by Eqs. (79) to (81) but with $\hat{u}_{ij}^{(1)}$ replacing the $\hat{u}_{ij}$.

The overall χ_1 is unchanged under the localized orbital transformation, Eq. (141), since everything else in Eq. (64) is invariant under this transformation. Then the values of E_2 and E_3 individually remain unchanged. The importance of the pairs part of E_3 relative to the three-electron correlations $R^{(3)}$ on the other hand is expected to increase.^{9b} The localized pairs (but not necessarily the van der Waals terms) should be more decoupled (independent) from one another than the MO pairs were. The same argument^{9b} applies to E_s and to E'_s , Eq. (82). It follows that a better energy and wave function would be obtained by minimizing the larger portion of the energy containing the variational localized pair energies to "all orders" (i.e. including $\langle \hat{\mu}_{vp}, m_{vp} \hat{\mu}_{vp} \rangle$) not just to the second order as in Eq. (157b). The resulting $\hat{\mu}_{vp}$ would give smaller R terms.

The details of such transformations applied to the whole of Eq. (82) are still under study.⁹¹ In the meanwhile, by analogy with Eqs. (86) and from a consideration of the environmental effects on a bond, ion core, etc., it may be assumed that the variational expression for a localized pair to "all orders" will be given by Eq. (162) below. In any case just E_2 alone may be sufficient so that one may work with Eqs. (157).

D. Effect of Molecular Environment on a Bond

Empirical bond energies are transferable from molecule to molecule, for example, in saturated hydrocarbons to within 0.01 eV². Are the detailed effects of molecular environment, implicit in the equations given above, compatible with such a constancy of bond energies?

The question of molecular environment again has a Hartree-Fock and a correlation part.

The localized orbitals of Eqs. (145) are affected by the potential V_ν of the entire H.F. "sea", i.e. of the molecule, and by the exclusion principle through orthogonality to all other η_ν 's and exchange terms. The V_ν combined with nuclear attractions causes the polarization of certain groups by electronegative atoms. Exchange and orthogonality cause the non-bonded repulsions.⁹² Both these and the V_ν effect due to shielding of the nuclei are of short range. The η_ν 's therefore are influenced mainly by their immediate environment. This orbital part of the problem has been investigated,^{35a,35b,35c,39} though more work seems necessary to see how localized the η_ν 's are and how constant.

The correlation part of a bond function, say $\hat{\mu}_{\nu\rho}^{(1)}$ (ν and ρ with the same spatial part), is also affected by the entire molecular H.F. "sea" ϕ_0 , though the $\hat{\mu}_{\nu\rho}$'s are nearly decoupled from each other in Eq. (157b).

As in the atomic case (Section XXIV) the environmental effects on $\hat{\mu}_{\nu\rho}^{(1)}$ through ϕ_0 are twofold:

(1) The V_ν in

$$e_\nu \equiv \left(-\frac{1}{2}\nabla_\nu^2 - \sum_I \frac{Z_I}{r_{I\nu}} \right) + V_\nu - \varepsilon_\nu \quad (12')$$

$$V_\nu(\mathbf{x}_\nu) = \sum_{k \geq 1}^N \langle k, g_{k\nu} (1 - P_{k\nu}) k \rangle_{\mathbf{x}_k} = \sum_k \bar{S}_k(\nu) \quad (8')$$

involve the Coulomb and exchange potentials of entire MO's, k . But using Eq. (141a), V_ν may be written in terms of the Coulomb and exchange potentials of the η_ν 's. It is then seen that the $Z/r_{I\nu}$ of a C—H bond ($\eta_\tau \alpha \eta_\tau \beta$) in ethane, for example, is shielded by the $S_\tau(\nu)$ of that bond. This shielded potential dies out before reaching the C—H bonds of the other methyl groups. To be sure

the C—H is only slightly shielded from the charge of its own carbon atom by the C—C electrons; however, in Section XXIV we saw how insensitive “dynamical” correlations are to changes in nuclear charge. Judging from the He, Li⁺, Be²⁺ (Table III)¹ and H₂ correlation values,¹ one would expect these ($V_v - Z/r$) type environmental effects on say a C—H bond not to be greater than 0.01 ev, the limit of constancy of experimental bond energies.

(2) The $\hat{\mu}_{vp}$ are orthogonal to the entire MO's, k [Eq. (157d)]. But from Eq. (141a) this leads to

$$\langle \hat{\mu}_{vp}, \eta_\tau \rangle = 0; \quad (\eta_\tau = \eta_1, \eta_2, \dots, \eta_v, \dots, \eta_\rho, \dots, \eta_N) \quad (160)$$

then, as with MO pairs (Section X), $\hat{\mu}_{vp}$ is orthogonal to its own η_v, η_ρ (like the f_i effect), but also to all other bonds η_σ ($\sigma \neq v, \rho$). The latter “exclusion effect” now represents the other environmental effect. It too is expected to be less than 0.01 ev for a C—H bond. Even in the lithium atom (Table IV), which has concentric electrons and hence more exclusion, 2s orthogonality affected ϵ_{12} of Li⁺ by only *ca.* 0.004 ev. The case of the $(1\sigma_g)^2 (1\sigma_u)^2$ Li₂ core (Section XXV) is similar. Equations (141b) turn this into $(1s_a)^2 (1s_b)^2$ as with the He—He case below. The ϵ_{vp} of these localized cores should then be like the ϵ_{12} of Li⁺ (−1.18 ev),¹ probably to within 0.01–0.02 ev.

From these considerations it would seem therefore that environmental effects, at least on the correlation part, are within the constancy of empirical bond energies. Correlation energies of lone pairs and ion-cores also seem transferable to this accuracy (~ 0.01 – 0.02 ev).

E. Calculation of a Bond Energy

Environmental effects being quite small, the correlation energy of a bond or lone pair can be calculated separately as though it were being calculated for say the H₂ molecule.

To the second order, one minimizes Eq. (157b) but replaces the $\sum_I Z_I/r_{Iv}$ and V_v in e_v 's by just the parts from that bond. Also, Eq. (157d) may be replaced by

$$\langle \tilde{\mu}_{vp}^{(1)}, \eta_\tau \rangle = 0 \quad (\tau = v, \rho) \quad (161)$$

where v and ρ differ only in their spin.

To all orders, the analog of Eq. (86) may be *assumed* to be

$$\epsilon'_{vp} \leq \tilde{\epsilon}'_{vp} \cong 2\langle \mathcal{B}(\eta_v \eta_\rho), g_{v\rho} \tilde{\mu}_{vp} \rangle + \langle \tilde{\mu}_{vp}, (e_v + e_\rho + m_{vp}) \tilde{\mu}_{vp} \rangle \quad (162)$$

where the $\tilde{S}_{vp}$ in m_{vp} involve only the potentials of η_v and η_ρ . Further work is needed to confirm this equation, however, unless one is content with just Eq. (157b) which presently is on a firmer basis.

The trial functions $\tilde{\mu}_{vp}$ may involve the r_{12} -coordinate like the James-Coolidge Junction^{93,78} for H_2 . In using such functions the $\mathcal{B}(\eta_v \eta_\rho)$ part is first split off according to Eqs. (104) to (106).

To calculate a bond energy *a priori* one also has to deal with the H.F. part of that bond alone. H.F. theory for localized groups is still in the developmental stage.^{41,42}

The variational form of $E_{H.F.}$ is

$$E_{H.F.} \leq \tilde{E}_{H.F.} \equiv \sum_{v=1}^N \langle \tilde{\eta}_v, h_v^o \tilde{\eta}_v \rangle + \sum_{v>\rho}^N \langle \mathcal{B}(\tilde{\eta}_v \tilde{\eta}_\rho), g_{v\rho} \mathcal{B}(\tilde{\eta}_v \tilde{\eta}_\rho) \rangle \quad (163)$$

from Eqs. (12), (143) and (144) and with trial orbitals $\tilde{\eta}_v$ such that

$$\langle \tilde{\eta}_v, \tilde{\eta}_\rho \rangle = \delta_{v\rho} \quad (164)$$

Again, combining the shielding terms and neglecting interactions between groups

$$\tilde{E}_{H.F.} \approx \sum_{\beta}^{N/2} \langle \mathcal{B}(\tilde{\eta}_\beta \tilde{\eta}_{\beta'}), (h_\beta^o + h_{\beta'}^o + g_{\beta\beta'}) \mathcal{B}(\tilde{\eta}_\beta \tilde{\eta}_{\beta'}) \rangle \quad (165)$$

where β and β' differ only in spin; h_β^o and $h_{\beta'}^o$ are the remaining parts of h_i^{eff} for just that bond. It may be possible to deal with a two-center-bond,² H.F. problem by minimizing a single pair in Eq. (165) keeping $\tilde{\eta}_\beta$ orthogonal to the inner shells and assuming a carbon ion core potential for the C—H h^o . This potential might then be improved by the use of $\tilde{S}_v$ of say the C—C bond orbital (e.g. in C_2H_6); or one may take the C—H part from CH_4 to calculate the C—C bond in C_2H_6 , C_3H_8 , etc. How practicable and accurate such procedures could be remains to be seen. They have been mentioned here only as possibilities.

Were Eq. (165) workable it would be combined with the correlation part to give

$$E_{\text{bond}} < \frac{\langle \psi_{\beta\beta'}, (h_\beta^o + h_{\beta'}^o + g_{\beta\beta'}) \psi_{\beta\beta'} \rangle}{\langle \psi_{\beta\beta'}, \psi_{\beta\beta'} \rangle} \quad (166)$$

with

$$\psi_{\beta\beta'} = \mathcal{B}(\eta_{\beta}\eta_{\beta'}) + \hat{\mu}_{\beta\beta'}$$

$$\langle \hat{\mu}_{\beta\beta'}, \eta_{\beta} \rangle = 0$$

Though the theory of the correlation part is available now, the actual calculation of a total bond energy by itself from such an equation as (166) must await the further development of molecular (localized) Hartree–Fock theory.

XXVIII. VAN DER WAALS ATTRACTIONS

It is customary to talk about van der Waals attractions between two atoms, say $\text{He} \cdots \text{He}$, in the Heitler–London (H.L.) description. The attraction near the minimum is due partly to the *distortion* of H.L. AO's (in the “orbital average polarization” effect),³ but especially at large internuclear distances r , it arises from simultaneous excitations in both atoms (the usual London dispersion force). The two effects have been compared⁹⁴ for H_2 in the triplet state as a function of r .

The distortion effect is automatically included in a Hartree–Fock calculation based on SCF MO's for the composite system of the interacting atoms. Ransil's⁹⁵ “best limited” H.F. SCF MO calculation gave the $\text{He} \cdots \text{He}$ interaction well, around the minimum (r_e), but gave too little attraction at (r/r_e) larger than about 1.2. The attraction at large r is an “intershell” correlation effect. This effect has been hitherto treated by the theory of London dispersion forces and applied also to the non-bonded attractions between different parts of a saturated molecule to obtain heats of formation and isomerization.²

The London theory uses second-order perturbation theory in its usual (R.S.) form: an infinite sum over a complete basis set. The set taken for the composite system of two interacting molecules a and b consists of all products $\psi_a^k \psi_b^l$ of the complete set of eigenfunctions of a and b separately. Thus, the London theory not only assumes that there is no overlap between the ground-state atoms but also that there is no overlap between any of the virtual atomic excited states.³

Consider, for example, two hydrogen atoms with the same spin, 3 Å apart.¹⁰ At this separation, overlap is indeed negligible between ground-state orbitals ($1s_a$)($1s_b$). But Bohr radii are

proportional to n^2 , so that even the next virtually excited state $(2p_z)_a(2p_z)_b$ that would contribute to the London force shows very large overlap. Thus, the usual derivation does not justify the use of London's formula even at considerable internuclear r 's. Then the intramolecular use of this formula too requires justification.^{3,90}

The experimental value of the coefficient of the r^{-6} term is smaller (more negative)² than the London value by a factor of 2.2 in Ne, Ar, Kr and Xe, but by only 1.2 for He and 1.09 in H₂. This was attributed by Donath and Pitzer² to higher order correlations than the second that became important in the larger atoms (see below).

McWeeny^{24b} extended the use of group functions, Eq. (146), to intermolecular forces by mixing to the second order a set of such many-electron functions Λ_A^K , Λ_B^L on each atom A and B, respectively. The functions of one atom A were assumed orthogonal in the sense of Eq. (1) not only to each other but also to those of B. There is no way of obtaining these functions. Also, the assumed Eq. (1) is too restrictive; between A and B it is equivalent³ to the no overlap assumptions of the London theory. These limitations were observed^{24a} on an application to He · · · He.

Many-electron theory^{3,90} gives the van der Waals attractions at all r both for inter- and intramolecular cases with no assumptions concerning overlap. It does not necessitate different starting points, or different theories, one for large r and another near r_e . It covers smoothly the difficult⁹⁶ intermediate region.

A. Intramolecular Attractions

The terms $\varepsilon_{\nu\rho}$, $\hat{\mu}_{\nu\rho}$, with ν and ρ referring to spatially different localized spin-orbitals, are for inter-group correlations. They are the generalization of the London-van der Waals attractions. However, $\hat{\mu}_{\nu\rho}$ is in a closed form, not expanded in atomic basis sets.

Equations (148) and (149) give the van der Waals attractions between localized groups if one has any function (such as H.F. and C.I.) $\phi_0 + \chi$ in the MO description. In this way, i.e. by the transformation to localized description, one can get for instance the correlation energy between two C—H bonds in CH₄.

Just the second-order part E_2 , Eq. (152), should be sufficient for calculating say isomerization energies with attractions between

bonds, e.g. (C—H), (C—H), etc. Each group has few electrons as in the $\text{He} \cdots \text{He}$ case, and the higher order corrections mentioned above,² e.g. for $\text{Ne} \cdots \text{Ne}$, are not needed. The use of London forces in hydrocarbons² is justifiable³ on the basis of Eq. (152) at least as far as the overlapping basis set problem and exclusion effects are concerned.

The van der Waals terms may be obtained separately without doing a calculation on the entire molecule. The inter-group pairs would need to be minimized in Eq. (157b) with trial functions $\tilde{\mu}_{\nu\rho}$. The relation between different $\hat{\mu}_{\nu\rho}$'s required so that χ will be of the proper symmetry (as discussed for atoms in Section XXIII) needs further investigation.⁹¹

Individual MO pair correlations, ε_{ij} , can be related to the localized ones, $\varepsilon_{\nu\rho}$, directly using Eq. (149). This may provide a semi-empirical method by which, from localized correlations which are easily estimated, MO pair correlations are obtained. Such a method may help ultraviolet spectral assignments based on simple MO theory by giving estimates of shifts due to correlation. $n-\pi^*$ transitions would be particularly interesting to consider.

B. Intermolecular Attractions

In dealing with intermolecular forces the many-electron theory again starts with H.F. SCF MO's, this time on the composite system of interacting molecules. In $\text{He} \cdots \text{He}$,⁹⁵ H.F. accounts for the gradual distortion of atomic orbitals $1s_a^\alpha$, $1s_a^\beta$, $1s_b^\alpha$, $1s_b^\beta$ into the equivalent orbitals $(\eta_1, \eta_2, \eta_3, \eta_4)$ at shorter r . Ransil's⁹⁵ H.F. ϕ_0 could be transformed⁴⁶ at various r to get these η 's. Nesbet has treated the N_2 molecule all the way to dissociation by the Hartree-Fock method directly in terms of equivalent orbitals.⁵

The same equivalent orbital transformation which applied to ϕ_0 works on the correlation part, Eqs. (77) and (153), of the wave function and energy as well and gives the generalized London-van der Waals terms at all r . These are the pairs in Eq. (152b) that have two localized orbitals η_ν and η_ρ with spatial parts on different molecules. Denoting the sum of all such intermolecular pairs by E_2^ω , we have

$$E_2^\omega = \sum_{\nu \geq 1}^{n_a} \sum_{\rho > n_a}^N \langle \mathcal{B}(\eta_\nu, \eta_\rho), g_{\nu\rho} \hat{\mu}_{\nu\rho}^{(1)} \rangle \quad (167)$$

where ω refers to the intermolecular van der Waals part; atom A contains n_a electrons and atom B n_b , so that $n_a + n_b = N$. There are $n_a n_b$ terms in Eq. (157). Even at short r we can speak of individual "molecules" or "atoms" if we consider the localized orbitals to be distorted forms of the orbitals of separated atoms or molecules.

In the MO pairs description the intra-atomic correlations are not sorted out from the inter-atomic ones. Thus, in a H.F. + MO C.I. calculation or in $\hat{u}_{ij}$ calculations most of the effort would go into obtaining the large intra-atomic correlations.* In the equivalent orbital description one may deal with just the inter-atomic pairs, Eq. (167), using Eq. (157b) [E_2^ω being a small quantity compared to the total E_2 , one would then have to calculate $\Delta^{(2)}$, Eq. (157c), too]. Intra-atomic correlations (as in He) are insensitive to the details of atomic orbitals (AO) and V_i . Hence, even at smaller r 's where the AO's are distorted into η 's, they are expected to cancel the purely atomic values at $r = \infty$.

The same spin inter-atomic pairs in Eq. (167) may sometimes be related to just one or a few of the $\hat{u}_{ij}$ pairs. For example, in $\text{He} \cdots \text{He}$

$$\hat{u}_{13} = -\hat{u}_{13} \quad (168a)$$

corresponding to

$$\mathcal{B}(1\sigma_g \alpha 1\sigma_u \alpha) = -\mathcal{B}(1s_a \alpha 1s_b \alpha) \quad (168b)$$

($\eta \rightarrow 1s$ as $R \rightarrow \infty$). This is because in Eq. (141) α spin-orbitals transform independently of β ones. The $\text{He} \cdots \text{He}$ case is particularly simple, there being no $\alpha\alpha$ intra-atomic pairs. The calculation of ε_{13} and ε_{24} is then just the same as obtaining the correlation energy of H_2 in the $^3\Sigma$ state.⁹⁴ At larger r , neglecting the difference between $\alpha\alpha$ and $\alpha\beta$ pairs,

$$E_2^\omega \approx 4\varepsilon_{13} \quad (169)$$

The use of $\hat{u}_{ij}$'s eliminates the overlap problem.

* This was recognized by Moffitt⁹⁷ and led to his theory of "atoms in molecules". However, he tried to obtain even the valence shell correlations from free atoms. Since valence electrons in a molecule do not preserve their atomic character, the idea of empirical intra-atomic correlation corrections applies properly only to inner shells (see also Section XXV).

Just E_2^{ω} alone gives the van der Waals attraction of $\text{He} \cdots \text{He}$ or $\text{H}_2 \cdots \text{H}_2$ to a sufficient accuracy. A comparison of the results obtained using the London form ($r \rightarrow \infty$) of E_2^{ω} and the data shows this.² But, for larger atoms, Ne, A, Kr, . . ., E_2^{ω} alone leads to a factor of 2.2 errors.² We investigate in the following paragraphs, therefore, the relation between the many-electron theory and the effects found by Donath and Pitzer² to account for this factor of 2. This will also show how the corrections may be calculated *at all* r , and without the London-type approximations.²

The errors apparently are *not* due to any corrections that would come in for each pair term $\varepsilon_{\nu\rho}$ in Eq. (167), such as continuum contributions to London's formula. These would also be proportional to $n_a \times n_b$ and give similar correction factors for He and H_2 as for Ne, A, etc.

The complete energy given by the many-electron theory includes R [Eqs. (78) to (80)]. These many-electron corrections are negligible compared to the total $E_{\text{corr.}}$ of an atom or the binding energy of a stable molecule (Section XVIII). The correlation energy, Eq. (167), *between* two non-bonded atoms on the other hand is a very small quantity to start with. The London attraction between two neon atoms² 4.0 Å apart ($r_e = 3.08$ Å) is only -1.3×10^{-3} ev as compared to the $E_{\text{corr.}} \approx -11$ ev of a single neon atom.¹ The R terms could then be easily comparable to E_2^{ω} . The examination of these R many-electron terms, therefore, becomes of particular importance in connection with intermolecular forces.

Assume* that Eqs. (141) and (145) transform Eq. (69a) into

$$\chi_1 \approx \sum_{\nu > \rho}^{N=n_a+n_b} \frac{\mathcal{A}}{\sqrt{2}} \left\{ (\eta_1 \eta_2 \cdots \eta_N) \frac{\hat{\mu}_{\nu\rho}^{(1)}}{(\eta_\nu \eta_\rho)} \right\} \quad (170)$$

and similarly for the χ_s and χ'_s of Eqs. (76) and (77). Then the energy can again be evaluated with diagrams as was done in Section XVIII with MO's. Aside from the $\Delta^{(2)}$, Eq. (157c), it would have the same form as Eqs. (159) and (79)–(81) but with i, j, k replaced by $\eta_\nu, \eta_\rho, \eta_\tau$.

* One-electron terms $\{\hat{f}_\nu\}$, corrections to η_ν , could also arise, unlike in the case of MO's.

With MO pairs one had [neglecting Eq. (81)]

$$E_3 \cong \text{diagram 1} + \text{diagram 2} \quad (171)$$

Similar diagrams may be drawn for the energy obtained from Eq. (170) in terms of localized orbitals. The diagrams now distinguish between intra- and inter-“atomic” terms. For example, for $\text{He} \cdots \text{He}$

$$E_3 \cong (\text{I}) + (\text{II}) + (\text{III}) + (\text{IV}) \quad (172)$$

$$(\text{I}) = \text{diagram A} + \text{diagram B} \quad (173)$$

$$(\text{II}) = \text{diagram} \quad (174)$$

$$(\text{III}) = \text{diagram} \quad (175)$$

$$(\text{IV}) = \text{diagram} \quad (176)$$

Equation (173) gives the higher order correction to the $E_{\text{corr.}}$ of each He "atom" [distorted into $(\eta_1\eta_2)$], Eq. (174) gives it to the interatomic $\epsilon_{vp}^{(2)}$. We have in Eq. (175), for example,

$$\langle \eta_1 \hat{\mu}_{24}^{(1)}, m_{12}^{\eta} \hat{\mu}_{14}^{(1)} \eta_2 \rangle \quad (175')$$

plus exchange terms negligible at large r . m_{12} indicates that orbital potentials $\tilde{S}$, Eq. (8') in Section XXVII-D, are for η_i 's.

The form of the energy obtained in the non-perturbation approximation, i.e. with χ_s , is similar. The $\hat{\mu}_{vp}^{(1)}$ in Eqs. (172) through (175') are replaced by $\hat{\mu}_{vp}$'s that minimize the complete pair energies, Eq. (162) including Eqs. (173) or (174), not just Eq. (157b).

The terms taken by Donath and Pitzer² [see their Eqs. (21) and (22)] correspond to E_2^{ω} , Eq. (167), and to Eq. (175) in the Heitler-London approximation ($r \rightarrow \infty$; overlap neglected). Their wave function contains no intra-atomic $\hat{\mu}_{vp}$ so that terms (I) and (IV) do not appear. In the additional dipole-dipole approximation which they make, (II) [not (IV) or (III)] vanishes.

The correction factor² $E_{\text{exp}}^{\omega}/E_{\text{London}}^{\omega}$ is 1.2 in He and 2.2 in Ne, A, Kr, Xe, N₂ and CH₄, where

$$E_2^{\omega} \cong E_{\text{London}}^{\omega} = - \frac{3\alpha_A \alpha_B I_A I_B}{2(I_A + I_B)r^6}$$

The number of diagrams of type (III) is

$$M_{\text{III}} = n_a(n_a - 1)n_b \quad (177)$$

vs. the number of pairs $n_a n_b$ in E_2^{ω} . Thus in He $\cdots$ He

$$\left(\frac{R_{\text{III}}}{E_2^{\omega}} \right)_{\text{He}} \propto \frac{4}{4}$$

whereas taking only the most polarizable $(np)^6$ electrons in Ne, A, Kr and Xe one has

$$\left(\frac{R_{\text{III}}}{E_2^{\omega}} \right) \propto \frac{180}{36}$$

Assuming roughly the same ratios for single diagrams, one sees from this that the correction factor should be *ca.* five times larger in the heavy atoms than in helium. The observed corrections are

in the ratio of about 1.2/0.2, i.e. six times.* It is difficult to understand, however, why the factor still remains about the same in N_2 and CH_4 .

Similar corrections to E_2^ω , Eq. (167), are given by the many-electron theory without the Heitler-London type approximations and therefore they are applicable at all r . The R_{III} , for example [Eq. (175')], can be calculated from η and the $\hat{\mu}_{rp}$ in closed form.

These terms may also be calculated from the $\hat{u}_{ij}$'s in the MO description. As mentioned in Section XXVII-C, the relative importance of the pairs, Eq. (173), to the triangles, Eqs. (175) and (176), part should be greater in the η description than in the MO one, Eq. (171). Nevertheless, owing to the simpler transformations of some pairs, as in Eq. (168), some of the MO triangles may correspond directly to R_{III} and possibly simplify its calculation. Further work is needed along these lines (see Note Added in Proof at the end of this article).

(I) and (III) seem to remain as the main terms in Eq. (172) at shorter r . Both (II) and (III) contain $\hat{\mu}_{24}\hat{\mu}_{24}(\approx\hat{\mu}_{24}\hat{\mu}_{14})$ but $m_{24}^\eta \ll m_{12}^\eta$. Hence we expect that (II) $\ll$ (III). The magnitude of (IV) (the effect of atomic correlation on the van der Waals attraction) should be checked; it is probably small since $\hat{\mu}_{12}$ and $\hat{\mu}_{24}$ are nearly orthogonal and m^η is weak. $\Delta^{(2)}$ in Eq. (157c) also needs to be calculated at shorter r (see Note Added in Proof).

To conclude this section, many-electron theory provides a way of calculating intermolecular attractions at all r directly,

* The R_{III} terms are positive, so that $E_2 + E_3$ or $E_2 + R_{III}$ gives *less* attraction than E_2^ω alone. This applies to the London formula *before the introduction of experimental polarizabilities*. On this basis, our equations are of the type of the Eqs. (24) and (26) of Reference 2 (p. 65), i.e.

$$E_{\text{exp}}^\omega \cong E_2^\omega + R_{III} \propto - \frac{h_A^2 h_B^2}{U_A + U_B} \cdot \frac{1}{r^6}$$

whereas

$$E_2^\omega \propto - \frac{h_A^2 h_B^2}{I_A + I_B} \cdot \frac{1}{r^6}$$

[E_2^ω , Eq. (167), reduces to the above r^{-6} form after the no-overlap and dipole-dipole approximations.]

Thus in the formulas without polarizabilities the correction factor comes from $I/U \cong 1/2.2$, whereas after the substitution of polarizabilities also with U_i 's, [$\alpha_i = 2h_i^2/U_i$], the factor is $U/I \cong 2.2$. The formulas containing the h_i^2 give $R_{III}/E_2^\omega \cong 0.2$ in He and 1.2 in Ne, A, etc. The empirical London formula² (U 's substituted everywhere for I 's in E_{London}) is different from E_2^ω .

though these are very small correlation effects on an absolute scale.

Hartree–Fock calculations on say just the $(2p)_a^6(2p)_b^6$ part of the composite Ne–Ne system remain as the crucial prerequisite for such larger systems. For the longer range part of the attraction one needs only the H.F. wave functions of the *separate atoms*; the corrections that would come from the use of *exact* atomic functions do not seem significant.

XXIX. RELATIVISTIC EFFECTS

We dealt above with the non-relativistic Schrödinger equation (2) and with the correlation energy defined as the difference between the exact solution of this and the Hartree–Fock energy.¹ With increasing nuclear charge Z , however, relativistic corrections are known⁹⁸ to become significant, in fact comparable to correlation energies at about $Z \approx 10$.

The main relativistic effects come not from the terms arising from $1/r_{ij}$ being made Lorenz invariant, but from the one-electron terms (H_1 and H_4) in Eq. (2) of Reference 98 (see also Reference 96). The increase in the mass of an electron at higher velocities causes, as in mesonic atoms, (i) tighter binding to nuclei and (ii) contraction of the orbits. These effects that come from the one-electron terms are included in the relativistic Hartree–Fock method.^{83,99}

For heavy atoms and molecules, many-electron theory can be made to start with relativistic equations. Though the exact relativistic Hamiltonian is not known it seems a good approximation to base the theory on the relativistic⁹⁹ Hartree–Fock Hamiltonian H_0 corrected by the non-relativistic $1/r_{ij}$ terms.

The relativistic many-electron theory can then be formulated in just the same way as in the non-relativistic case above; the “relativistic” χ can be obtained and various shells and electron groups separated in it. Because of their strong Z^* (effective nuclear charge) dependence, relativistic effects will then be confined mainly to the inner shells⁹⁹ and will cancel out in the calculations of molecular binding energies and other valence electron properties. Further approximations may then be made in the formal relativistic theory for the outer shell parts of χ_{rel} and E_{rel} to get the non-relativistic equations of this article.

Though relativistic effects are mainly important for the inner shells, they have the following indirect effect on the outer electrons.

One can minimize the energy of just a valence shell to obtain its wave function both in the H.F. part and the $\hat{u}_{ij}$'s provided the trial functions are kept orthogonal to the inner orbitals [see Eqs. (86) and (99b)]. The relativistic shrinkage of the inner shells and the shell structure then causes the outer electrons to shrink too. Thus, even to calculate the *non*-relativistic valence shell, a knowledge of the inner orbitals is needed. These may probably be approximated by the relativistic H.F. orbitals obtained from the actual free ions corresponding to the cores. The "medium" potential V is also affected by them, and hence by relativistic effects. However, the $\hat{u}_{ij}$ parts of the outer wave function are not sensitive to changes in V_i .

A formalism starting relativistically would allow errors that would arise from further approximations on the non-relativistic outer shells to be estimated.

XXX. CONCLUSION

We started with the exact wave function and energy of a many-electron system without an orbital basis set or a perturbation expansion. These consist of a Hartree-Fock part and the remaining correlations between progressively larger numbers of electrons. The main correlation effects were found to be for all pairs of electrons. They are obtained *by any of the available two-electron methods*, e.g. those on He or H_2 , depending on the nature of the pair as discussed in Section XXII. Remaining effects, i.e. changes of orbitals due to correlation and n -electron correlations ($n > 2$), are estimated as minor errors from Eqs. (90) and (79).

The "successive partial orthogonalizations" method (Section IX) that led us to the detailed form of the exact w.f. can also be used on any variational many-electron trial function which may not be amenable to any physical or chemical interpretation to start with. This method of partial integrations not only makes the orbitals and the various correlation effects inherent in this trial function explicit, but also shows how to improve the trial function very simply.

The "many-electron theory" puts the separate treatment of (i) inner-outer, e.g. σ , π , shells, and (ii) localized bonds, lone pairs and ion cores on a rigorous basis both for semi- and non-empirical calculations. It shows how the following may be calculated to chemical accuracy by properly dealing with electron correlation:

- (a) molecular binding energies;
- (b) an individual bond energy within a large molecule;
- (c) intra-molecular van der Waals attractions, hence conformational energy changes in molecules;
- (d) intermolecular van der Waals forces over the whole range of internuclear distances;
- (e) electronic spectra.

The methods do not become rapidly difficult as the number of electrons or the size of a molecule increases.

The theory developed should allow one to calculate the binding energy of a heavy molecule such as Na_2 by dealing with only its valence electrons and in almost the same way as in a James-Coolidge type H_2 calculation. We believe that such calculations on large systems are possible today with no more numerical effort than is currently being expended on first row molecules in many laboratories.

Further work and applications are needed on Hartree-Fock methods for dealing with portions of large systems, on the many-electron theory of non-closed shells and on *intra*-molecular van der Waals forces.

Thanks are due to numerous colleagues who through valuable comments and questions contributed much to this work. The help of N. R. Kestner, V. McKoy and D. F. Tuan in the final revision of the manuscript is gratefully acknowledged.

Part of this work was done during visits to the Chemistry Departments of Harvard University and Orta-Doğu Teknik Üniversitesi (Middle East Technical University) of Ankara, Turkey. The writer is indebted to the staffs of both departments for their hospitality.

Note Added in Proof

While this review was in press the following developments concerning the many-electron theory took place:

1. The method of "successive partial orthogonalizations"

(Section IX) was shown to yield not only the various terms of χ , but also the Hartree-Fock orbitals themselves [O. Sinanoğlu, *Rev. Mod. Phys.* **35**, 517 (1963) (issue dedicated to Sanibel Island Symposium in Honor of E. A. Hylleraas; Jan. 1963)]. Thus from an arbitrary trial function $\tilde{\psi}$, if it is sufficiently accurate, one can extract the H.F. orbitals without requiring a separate variational calculation. The method was applied to a three-term Hylleraas r_{12} -type w.f. of helium and accurate H.F. orbitals were obtained on a desk calculator (see N. R. Kestner, *J. Chem. Phys.*, **39**, 1361 (1963)).

2. As a demonstration and further check of the theory, detailed machine calculations were performed on the Be atom (D. F. Tuan and O. Sinanoğlu, *J. Chem. Phys.*, to be published). The tentative results are $\varepsilon_{12} = -1.175$ ev, $\varepsilon_{34} = -1.132$ ev. The intershell correlation $4\varepsilon_{1s2s}$ and the R triangles are being evaluated. The former is approximately^{4,67} (-0.2 ev); R is expected^{9a} to be <0.01 ev. Our $E_{\text{corr.}}$ with ε_{12} and ε_{34} only is 89.16 % of the total correlation energy. Watson's⁶⁵ 37-term C.I. calculation (including all effects) yields 89.36 % of the total correlation.

3. The $\text{He} \cdots \text{He}$ interaction was calculated over a wide range of interatomic distances ($r > 2$ A). One calculation gave a very accurate nonempirical value for the coefficient of the long range term r^{-6} . The value is $c = -1.540$ a.u. compared with Dalgarno's and Kingston's [*Proc. Phys. Soc. (London)*, **73**, 455 (1959); **78**, 607 (1961)] "experimental" value $-1.50 \pm 10\%$. The many-electron effects (Section XXVIII above) contributed 6.7% to c . In a less accurate calculation limited by the available Hartree-Fock, the relative magnitudes of various effects and diagrams discussed in Section XXVIII above were obtained as a function of r . At the minimum of the potential at r_0 , many-electron and distortion effects were 9%. This first test calculation using Slater orbitals for the crude Hartree-Fock part and the simplest pair functions already gave a potential minimum of depth 5.24°K at 3.08 A [*Bull. Am. Phys. Soc.*, **8**, 535 (1963)]. "Experimental" values vary; Buckingham's "best values" are 9.63°K and 2.88 A. The values would definitely be improved by the use of accurate Hartree-Fock MO's or even LCAO MO's built of atomic Hartree-Fock orbitals and with more complete pair trial functions. Adding some corrections to the calculated results, Kestner obtains a new potential with a depth of 9.92°K ($\pm 10\%$) at 2.98 A.

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IONIC SOLVATION

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I. INTRODUCTION

The properties of ions in media of high density are of considerable interest, and the way in which the interactions between ions and solvent molecules affect the macroscopic properties of

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electrolyte solutions is not perfectly understood. Considerable progress has been made in the theory of electrolyte solutions; however, all current theories start from the Coulomb macroscopic law

$$q_{\alpha}q_{\beta}/\varepsilon R_{\alpha\beta} \quad (1)$$

as expressing the potential of the average force, or effective interaction, between two ions α and β of charges q_{α} , q_{β} , imbedded at a relative distance $R_{\alpha\beta}$ apart in a solvent of macroscopic dielectric constant ε . Moreover, the superposition approximation is usually introduced. Whereas Eq. (1) may be a useful approximation, clearly it is not exact, and it can be surmised that a more general expression of the type

$$A_1R^{-1} + A_2R^{-2} + \dots \quad (2)$$

would better represent the actual effective interaction.

On the other hand, the ion-solvent interactions manifest themselves directly in the magnitude of the free energy of solvation. Free energies of solvation (or hydration) of salts have been frequently discussed and correlated. These quantities are also of interest because they are directly related to the chemical potentials of ions at infinite dilution, which, in turn, together with the chemical potential of the undissociated molecule, govern the dissociation equilibrium at infinite dilution.

Both the potential of the average force and the thermodynamic quantities related to solute particles at infinite dilution can in principle be calculated within the framework of classical statistical mechanics. Formal relations have been derived by McMillan and Mayer¹ and discussed by Hill.² We shall discuss them briefly in Section III.

Nevertheless, no attempt has been made until quite recently to discuss Eq. (1) in terms of statistical-mechanical expressions.

The basis for a statistical-mechanical treatment of ionic solvation is outlined below. Some explicit calculations are also included.

As usual, the relevant quantities are expressed in terms of the intermolecular potential energy of the whole system. Accordingly, we begin with a discussion of the total energy of a system composed of molecules and ions.

II. INTERMOLECULAR POTENTIAL ENERGY OF A SYSTEM OF MOLECULES AND IONS

A. Conventional Distinction between Types of Interaction

The intermolecular potential energy of a pair of molecules i, j is represented as a function of the relative distance r_{ij} and the mutual orientations ω_i, ω_j . It is customary to consider the following contributions, which are supposed to be additive:

(i) The repulsion of electronic shells, acting at very small distances.

(ii) The London dispersion forces, varying as r_{ij}^{-6} or faster.

(iii) Electrostatic forces. Their contribution is given by³

$$\iint d\mathbf{r}_1 d\mathbf{r}_2 \frac{\rho_i(\mathbf{r}_1)\rho_j(\mathbf{r}_2)}{|\mathbf{r}_1 - \mathbf{r}_2|} \quad (3)$$

where $\rho_i(\mathbf{r}_1)$ and $\rho_j(\mathbf{r}_2)$ are the charge distributions of the molecules i and j . If ρ_i and ρ_j are expanded in a system of spherical harmonics, expression (3) can be transformed into a power series in r_{ij}^{-1} . If the charge distributions do not overlap, the terms represent the interactions of external electric moments of charge distribution, called multipoles. The first is the net charge, the second the familiar dipole moment, etc. If the molecules have no spherical or cylindrical symmetry, quite complicated functions of the Eulerian angles specifying the orientations of molecules can arise. For the ion-molecule interaction, the first term is the charge-dipole term, given by

$$q_i \mu_j r_{ij}^{-2} \cos \theta_j \quad (4)$$

It can be conveniently represented as

$$q_i \mathbf{s}_{ij} \boldsymbol{\mu}_j \quad (5)$$

where $\boldsymbol{\mu}_j$ is the dipole moment vector of the molecule j and

$$\mathbf{s}_{ij} = \nabla_j \left(\frac{1}{r_{ij}} \right) = - \frac{\mathbf{r}_{ij}}{r_{ij}^3} \quad (6)$$

The next term is the ion-quadrupole contribution of the form

$$q_i r_{ij}^{-3} \sum_{m=-2}^{+2} \frac{(2 - |m|)!}{(2 + |m|)!} P_2^m(\cos \theta_j) e^{-im\phi_j} Q_2^m(j) \quad (7)$$

where P_l^m are associated Legendre polynomials, θ_j and ϕ_j specify the orientation of molecule j and Q_2^m are linear combinations of components of the quadrupole second-order tensor. In general, the electrostatic interaction between a spherical ion and a molecule can be represented as

$$q_i v(r_{ij}, \omega_j; \rho_j) \quad (8)$$

For a pair of electrically neutral molecules, the first term is the dipole-dipole term, varying as r_{ij}^{-3} , which can be represented as

$$\mu_i \mathbf{T}_{ij} \mu_j \quad (9)$$

where the second-order tensor,

$$\mathbf{T}_{ij} = -\nabla_i \nabla_j \left(\frac{1}{r_{ij}} \right) = \frac{1}{r_{ij}^3} \left(\mathbf{U} - 3 \frac{\mathbf{r}_{ij} \mathbf{r}_{ij}}{r_{ij}^2} \right) \quad (10)$$

describes the interaction between the dipoles μ_i and μ_j . $\mathbf{U}$ is the unit tensor. The dipole-quadrupole and quadrupole-quadrupole contributions vary as r_{ij}^{-4} and r_{ij}^{-5} , respectively.

Contributions varying as r_{ij}^{-1} , r_{ij}^{-2} and r_{ij}^{-3} are called here the long-range ones. The usual integrals, over the coordinates of molecules confined to a macroscopic volume V of the system, cannot be extended to infinite space, as is always permissible when only short-range forces are present. This reflects the fact that long-range forces can give rise to shape-dependent quantities, i.e., quantities which depend on the shape of the volume V . Therefore the long-range contributions should be extracted and dealt with separately.

(iv) Deformation effects.⁴ In Eq. (3), ρ_i and ρ_j are actual distributions of electron clouds and nuclei, already differing from the charge distributions in isolated molecules owing to deformation effects. The principal effect is the well-known one in which the electrostatic field due to the molecule i induces an induced dipole moment in the other molecule. At low field strengths, the induced moment is proportional to the field:

$$\mathbf{m}_j = \alpha_j \mathbf{E} \quad (11)$$

The tensor α is the well-known polarizability tensor. The potential energy of the system of two molecules is increased by

$$-\frac{1}{2} \mathbf{E} \cdot \alpha \cdot \mathbf{E} \quad (12)$$

In the neighbourhood of an ion, where the field is strong, the polarizability is probably no longer independent of the field; moreover, the field varies rapidly and higher moments are also induced. Not much is known, however, about these "hyperpolarizabilities", and we shall take into account only the polarizability α of molecules and ions.

B. Potential Energy of a System of Ions and Non-polar Molecules

Let us consider a system of N spherical particles, molecules or ions, of polarizability α_i and charge q_i . The potential energy due to the short-range contributions of the dispersion and repulsion forces is supposed to be independent of the electrostatic long-range forces. In a given spatial configuration, described by a set of position vectors $\{\mathbf{r}^N\} = \{\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N\}$, the induced dipole moment of the particle i is

$$\mathbf{m}_i = \alpha_i \mathbf{E}(\mathbf{r}_i) \quad (13)$$

where the field $\mathbf{E}(\mathbf{r}_i)$ is that due to all the other particles. At a point $\mathbf{r}_i$ the field due to a charge q_j located at $\mathbf{r}_j$ is

$$\mathbf{s}_{ij} q_j \quad (14)$$

and the field due to a dipole $\mathbf{m}_j$ at $\mathbf{r}_j$ is

$$-\mathbf{T}_{ij} \mathbf{m}_j \quad (15)$$

Therefore

$$\mathbf{E}(\mathbf{r}_i) = \sum_{j, j \neq i} \mathbf{s}_{ij} q_j - \mathbf{T}_{ij} \mathbf{m}_j \quad (16)$$

The electrostatic energy of the whole system is composed of charge-charge, charge-dipole, dipole-dipole, and deformation energy

$$U_{\text{el}} = \sum_{i < j} \sum \frac{q_i q_j}{r_{ij}} - \sum_{i \neq j} \mathbf{m}_i \mathbf{s}_{ij} q_j + \sum_{i < j} \mathbf{m}_i \mathbf{T}_{ij} \mathbf{m}_j - \frac{1}{2} \sum_i \mathbf{E}(\mathbf{r}_i) \cdot \alpha_i \cdot \mathbf{E}(\mathbf{r}_i) \quad (17)$$

We neglect terms of higher order. Expression (17), being formally correct, is practically useless and has to be transformed. This

is most conveniently done by introducing the following $3N$ -dimensional vectors and $3N \times 3N$ -dimensional tensors

$$\begin{aligned}
 \mathcal{M} &= \{\mathbf{m}_i\} \\
 \mathcal{E} &= \{\mathbf{E}_i\} \\
 \mathcal{S} &= \{\mathbf{S}_i\} \\
 \mathbf{T} &= \{\mathbf{T}_{ij}\} \\
 a &= \{\boldsymbol{\alpha}_i\}
 \end{aligned}
 \quad
 \begin{aligned}
 \mathbf{S}_i &= \sum_j \mathbf{s}_{ij} q_j; \quad \mathbf{s}_{ii} = 0 \\
 \mathbf{T}_{ii} &= 0
 \end{aligned}
 \tag{18}$$

With these definitions, and introducing

$$\mathcal{A} = (\mathbf{U} + a\mathbf{T})^{-1} \cdot a \tag{19}$$

we transform⁵ Eq. (17) into:

$$U_{\text{el}} = -\frac{1}{2} \mathcal{S} \cdot \mathcal{A} \cdot \mathcal{S} + \sum_{i < j} \frac{q_i q_j}{r_{ij}} \tag{20}$$

For a system containing N_0 molecules of polarizability $\boldsymbol{\alpha}_0$ and N_α ions labelled $\alpha, \beta, \dots, \varepsilon$, so that $N = N_0 + N_\alpha$ we have

$$\left. \begin{aligned} q_i &= 0 \\ \boldsymbol{\alpha}_i &= \mathbf{U} \boldsymbol{\alpha}_0 \end{aligned} \right\} \quad i \leq N_0$$

$$\left. \begin{aligned} q_i &= q_\alpha \\ \boldsymbol{\alpha}_i &= \boldsymbol{\alpha}_\alpha \end{aligned} \right\} \quad N_0 < i \leq N; \quad \alpha = \alpha, \beta, \dots, \varepsilon$$
(21)

We note that the total potential energy can be represented as

$$U = U_{\text{sh}} + U_{\text{el}} \tag{22}$$

where the first term can be interpreted as the potential energy of a system containing discharged ions (all q 's equal to zero). Accordingly, we write

$$U = U(\mathbf{q}) = U(0) + U_{\text{ch}}(\mathbf{q}) \tag{23}$$

where $\mathbf{q} = \{q_\alpha, q_\beta, \dots, q_\varepsilon\}$.

C. Potential Energy of a System of Ions and Polar Molecules

The equations of the preceding section can be generalized so as to include the permanent dipole moments of the molecules. The final expression⁵ is similar to the equation given by Mandel

and Mazur⁶ for a system of polarizable dipolar molecules in an external homogeneous electric field. We shall not quote this equation here, because it has not been applied in further calculations. No calculation of the static dielectric constant has been attempted for such a model either. Therefore, we shall discuss below the limiting case of polar rigid non-deformable molecules. Indeed, for such a case, if pair-wise additivity of intermolecular potentials is assumed as usual, the expression for the total potential energy simplifies notably and we can write:

$$U = \sum_{i < j} \sum u_{ij}; \quad i, j = 1, 2, \dots, N_0 \quad (24)$$

We divide U into ion-ion, ion-solvent and solvent-solvent interactions, and next subdivide each term into "non-electrostatic" (short-range) terms and "electrostatic" terms. In general, the electrostatic terms contain short-range as well as long-range terms; e.g., the dipole-dipole interaction is a long-range term, and the dipole-quadrupole is in fact a short-range one, as it varies as r_{ij}^{-4} . We can rewrite Eq. (24) as:

$$U = U_{\text{sh}} + \sum_{\alpha} \sum_i q_{\alpha} v_{\alpha i}(r_{\alpha i}, \omega_i) + \sum_{i < j} u_{ij}^{\text{el}}(r_{ij}; \omega_i, \omega_j) + \sum_{\alpha < \beta} \frac{q_{\alpha} q_{\beta}}{R_{\alpha\beta}} \quad (25)$$

The first and third terms represent the potential energy of a system containing discharged ions; the second and the last ones can be called the energy of charging the ions. The subscripts i and j are here relative to the N_0 molecules, and α and β to the N_{α} ions. Accordingly we rewrite (25) as

$$U(q) = U(0) + U_{\text{ch}}(\mathbf{q}, \mathbf{r}^{\alpha}; \mathbf{r}^{N_0}; \omega^{N_0}) \quad (26)$$

In the energy of a system with discharged ions only the dipole-dipole term is long-range. We note that U_{ch} is bilinear in the ionic charges in the term representing the direct charge-charge Coulomb interaction, and linear in the ionic charges in the remaining term, which represents simply the sum of the ion-solvent interactions.

We shall also discuss below the simple case of a slightly polar solvent of spherical molecules with embedded rigid point dipoles;

in such a case, and when the ions are spherical, $U(0)$ can be represented as

$$U(0) = U_0(0) + \sum_{i < j} \mathbf{m}_i \mathbf{T}_{ij} \mathbf{m}_j \quad (27)$$

and

$$U_{\text{ch}}(\mathbf{q}) = \sum_{\alpha < \beta} \sum \frac{q_\alpha q_\beta}{R_{\alpha\beta}} + \sum_{\alpha} q_\alpha \sum_i \mathbf{s}_{\alpha i} \mathbf{m}_i \quad (28)$$

III. FREE ENERGY OF CHARGING A SET OF IONS

We are now in a position to express the potentials of the average force in terms of molecular quantities entering through the total potential energy discussed above. First, we shall assume that the contributions of internal degrees of freedom and of kinetic translational and rotational ones are fully separable from the intermolecular potential energy. Under this assumption these contributions cancel out. Secondly, the potentials of the average force and the free energy of solvation are formally defined by identical equations for charged and for neutral particles. Since U contains short-range terms, the potential of the average force contains contributions of a short-range character similar to those found in solutions of neutral molecules. We should note that these quantities are not known even for binary solutions of neutral molecules, as the explicit calculations would be extremely difficult for dense media. Of primary interest in ionic solutions are the electrostatic effects, which are directly related to ionic charges. Therefore we postpone from the beginning any attempt to calculate the contributions to the potentials of the average force of the usual short-range intermolecular interactions; accordingly, we can express the potentials of the average force and the free energy of solvation in terms of the free energies of charging the sets of ions.

A. General Relations and Potentials of the Average Force

Consider a system of N solvent molecules (N replaces N_0 of Section II) and N_α ions $\alpha, \beta, \gamma, \dots, \varepsilon$ at a given temperature T and volume V . McMillan and Mayer¹ have shown that the

thermodynamic and statistical quantities referring to a solution of finite concentration can be related to distribution functions and potentials of the average force *at infinite dilution*. The potential of the average force at infinite dilution, relative to a group of N_α solute particles (no other solute particles being present), is defined as follows

$$\exp [-\beta \mathcal{W}(N, N_\alpha)] = \frac{\iint d\mathbf{r}^N d\boldsymbol{\omega}^N \exp [-\beta U(N + N_\alpha)]}{\iint d\mathbf{r}^N d\boldsymbol{\omega}^N \exp [-\beta U(N)]} \quad (29)$$

This is valid for T, V, N constant and under the assumption of a cancellation of contributions to the free energy other than U . $U(N + N_\alpha)$ stands for the total intermolecular potential energy of the system, and $U(N)$ for that of the pure solvent. The integration is carried out within the phase space accessible to solvent configurations. The denominator is simply equal to

$$\exp [-\beta F_0] \quad (30)$$

where F_0 is the configurational part of the free energy of the pure solvent.

$\mathcal{W}$ is called the potential of the average force, because the average force acting on a solute particle, say γ , in a given configuration of the set of N_α solute particles is obtained from $\mathcal{W}$ by taking the respective gradient. This force is averaged over all solvent configurations. Differentiating (29) we can verify that

$$\frac{\partial \mathcal{W}}{\partial \mathbf{r}_\gamma} = -\bar{\mathbf{F}}_\gamma = \frac{\overline{\partial U}}{\partial \mathbf{r}_\gamma} = \frac{\iint \frac{\partial U}{\partial \mathbf{r}_\gamma} \exp [-\beta U] d\mathbf{r}^N d\boldsymbol{\omega}^N}{\iint \exp [-\beta U] d\mathbf{r}^N d\boldsymbol{\omega}^N} \quad (31)$$

$$[U = U(N + N_\alpha)]$$

If U is divided into $U(0)$ and U_{ch} [cf. Eqs. (23) and (26)], $\mathcal{W}$ can be represented as:⁵

$$\mathcal{W} = W(0) + W_{\text{ch}} \quad (32)$$

with

$$W_{\text{ch}} = -kT \ln \frac{\int \int d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(0)] \exp[-\beta U_{\text{ch}}]}{\int \int d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(0)]} \quad (33)$$

$$W(0) = -kT \ln \frac{\int \int d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U(0)]}{\int \int d\mathbf{r}^N d\boldsymbol{\omega}^N \exp[-\beta U_N]} \quad (34)$$

The first term, W_{ch} , can be called the *free energy of charging the set of ions*, held in fixed positions; $W(0)$ is the potential of the average force for discharged ions. We limit our discussion to W_{ch} .

B. Irreducible Interactions⁷

The total potential of the average force can be decomposed into a sum of contributions of single ions, pairs, triplets, etc. If we denote $\mathcal{W}$ for one ion by

$$\mathcal{W}(\mathbf{r}_\alpha) = w_1(\mathbf{r}_\alpha) = w_1^{(\alpha)} \quad (35)$$

we have for two ions

$$\mathcal{W}(\mathbf{r}_\alpha, \mathbf{r}_\beta) = w_1^{(\alpha)} + w_1^{(\beta)} + w_2^{(\alpha\beta)} \quad (36)$$

and this equation defines w_2 . Similarly, for three ions

$$\mathcal{W}(\mathbf{r}_\alpha, \mathbf{r}_\beta, \mathbf{r}_\gamma) = \sum_{\alpha} w_1^{(\alpha)} + \sum_{\alpha < \beta} w_2^{(\alpha\beta)} + w_3^{(\alpha\beta\gamma)} \quad (37)$$

and this equation defines w_3 . In general

$$\mathcal{W}(\mathbf{r}^x) = \sum_{\text{singlets}} w_1^{(\alpha)} + \sum_{\text{pairs}} w_2^{(\alpha\beta)} + \sum_{\text{triplets}} w_3^{(\alpha\beta\gamma)} + \dots + w_n^{(\alpha\beta\cdots\epsilon)} \quad (38)$$

The quantities w_n can be called irreducible potentials, as they represent the interactions of the set of n ions which cannot be reduced to interactions of smaller sets of ions.

The free energy of charging a set of ions can be similarly decomposed. This decomposition is unambiguous if the ions are fairly distant from one another. In fact, we can write for one ion

$$W_{\text{ch}}(\mathbf{r}_\alpha) = w_1^{(\alpha)}$$

and this quantity is independent of $\mathbf{r}_\alpha$. For two ions we have

$$W_{\text{ch}}(\mathbf{r}_\alpha, \mathbf{r}_\beta) = w_1^{(\alpha)} + w_1^{(\beta)} + w_2^{(\alpha\beta)}$$

and $w_2^{(\alpha\beta)}$ contains the difference between $w_1^{(\alpha)}$ (when only the ion α was initially present in the discharged state) and the work of charging α in the presence of the discharged ion β at $\mathbf{r}_\beta$, as well as a similar difference for the ion β . This difference gives rise to short-range terms in w_2 which will probably become significant when α and β are close to one another. Bearing this in mind, we can nevertheless decompose W_{ch} for a set of ions into a sum of w_n 's, which are also related to irreducible interactions.

Obviously we can expect a relation

$$w_n = w_n + (\text{short-range terms})$$

to hold.

C. Expansion in Powers of Ionic Charge⁵

The general expression for W_{ch} can be treated according to standard techniques of statistical mechanics. We discuss below the perturbation treatment, in which the system containing the set of discharged ions is chosen as the unperturbed state. When the Boltzmann factor is expanded in a power series:

$$\exp[-\beta U_{\text{ch}}] = \sum_{n=0}^{\infty} \frac{(-\beta)^n}{n!} U_{\text{ch}}^n \quad (39)$$

and use is made of the formula

$$\ln(1 + X) = \sum_{k=1}^{\infty} \frac{(-X)^k}{k}, \quad |X| < 1 \quad (40)$$

a power series in β is obtained

$$W_{\text{ch}} = \sum_{l=1}^{\infty} \frac{(-\beta)^{l-1}}{l!} \lambda_l \quad (41)$$

where λ_l are the well-known Thiele semi-invariants, which are polynomials in terms of the moments. The n th moment is

$$m_n = \overline{(U_{\text{ch}})^n} \quad (42)$$

where the bar denotes a canonical average over the unperturbed system. The first two semi-invariants are:

$$\lambda_1 = m_1; \quad \lambda_2 = m_2 - m_1^2 \quad (43)$$

In general:

$$m_{k+1} = \sum_{r=0}^k \binom{k}{r} \lambda_{k-r+1} m_r \quad (44)$$

The average can be expressed in terms of integrals with distribution functions referring to the unperturbed state as weighting factors. Accordingly, let us introduce the following functions;

the specific probability density:

$$P(0) = \exp[-\beta U(0)] / \int \int \exp[-\beta U(0)] d\mathbf{r}^N d\boldsymbol{\omega}^N \quad (45)$$

the generic distribution functions:

$$\rho^{(h)}(\mathbf{r}^h, \boldsymbol{\omega}^h) = \frac{N!}{(N-h)!} \int P(0) d\mathbf{r}_{h+1} d\boldsymbol{\omega}_{h+1} \dots d\mathbf{r}_N d\boldsymbol{\omega}_N \quad (46)$$

the spatial distribution functions, averaged over rotational coordinates:

$$\eta^{(h)}(\mathbf{r}^h) = \int \rho^{(h)}(\mathbf{r}^h, \boldsymbol{\omega}^h) d\boldsymbol{\omega}^h \quad (47)$$

the correlation functions γ :

$$\eta^{(h)}(\mathbf{r}^h) = \gamma^{(h)}(\mathbf{r}^h) \prod_{i=1}^h \eta^{(1)}(\mathbf{r}_i) \quad (48)$$

all referring to solvent molecules in a system containing discharged ions. These distribution functions can be compared with the corresponding quantities in the pure solvent:

$$P_0(0) = \exp[-\beta U(N)] / \int \int \exp[-\beta U(N)] d\mathbf{r}^N d\boldsymbol{\omega}^N \quad (49)$$

$$\rho_0^{(h)}(\mathbf{r}^h, \boldsymbol{\omega}^h) = \frac{N!}{(N-h)!} \int P_0(0) d\mathbf{r}_{h+1} d\boldsymbol{\omega}_{h+1} \dots d\mathbf{r}_N d\boldsymbol{\omega}_N \quad (50)$$

$$n^{(h)}(\mathbf{r}^h) = \int \rho_0^{(h)} d\boldsymbol{\omega}^h \quad (51)$$

$$n^{(h)}(\mathbf{r}^h) = [n^{(1)}]^h g^{(h)}(\mathbf{r}^h) \quad (52)$$

The quantities $\rho^{(h)}$, $\eta^{(h)}$ can in principle be expressed in terms of $\rho_0^{(h)}$, $n^{(h)}$ and the difference $U(0) - U_N$. The corresponding cluster-like expansion has been given by Kirkwood and Salsburg.⁸

Now, U_{ch} contains terms linear and bilinear in the ionic charges. The direct Coulombic interaction between ions appears in the first semi-invariant and cancels out in all higher ones. The remaining part of U_{ch} is bilinear in non-polar solvents and linear in solvents of rigid molecules. Accordingly, λ_i contains products of ionic charges of total powers $2l$ and l , respectively. Hence in non-polar solvents, λ_1 contributes to w_1 and also to w_2 . The macroscopic approximation to w_2 , which is proportional to $q_\alpha q_\beta$ [cf. Eq. (1)], is therefore an approximation to λ_1 ; all higher λ 's, if different from zero, are corrections to the macroscopic law (1). Similarly, for polar solvents, (1) comes out of the second semi-invariant, λ_2 . Higher semi-invariants give corrections to (1).

We shall be concerned below with the following questions. First, we want to show how Eq. (1) can result from statistical-mechanical relations for w_2 and what approximations have to be introduced. Since (1) contains the macroscopic static dielectric constant for the pure solvent, ϵ , we have to make use of statistical-mechanical expressions for ϵ in terms of molecular quantities—more strictly, in terms of properties of molecules and intermolecular forces. This limits our discussion to fairly simple models of solvents.

Secondly, we attempt an explicit calculation of w_2 and w_3 ; this can also be done only for very simple solvent models.

As a “by-product”, the free energy of charging a single ion can be calculated by a very similar treatment. In the last section we shall describe an attempt to calculate w_1 explicitly, thus also evaluating the contribution of dielectric saturation—for a very simple solvent model, of course.

IV. POTENTIAL OF THE AVERAGE FORCE IN A NON-POLAR SOLVENT

A. Derivation of the Coulomb Macroscopic Law for Two Ions

Let us consider two ions, α and β , situated at $\mathbf{r}_\alpha$ and $\mathbf{r}_\beta$ at a distance $R_{\alpha\beta} = |\mathbf{R}_{\alpha\beta}| = |\mathbf{r}_\beta - \mathbf{r}_\alpha|$ apart. The explicit form for U_{ch} is [cf. Eq. (20)]:

$$U_{\text{ch}} = q_\alpha q_\beta / R_{\alpha\beta} - \frac{1}{2} \mathcal{S} \mathcal{A} \mathcal{S} \quad (53)$$

The tensor $\mathcal{A}$ is expanded as follows

$$\mathcal{A} = a - a\mathbf{T}a + a\mathbf{T}a\mathbf{T}a - \dots + \dots \quad (54)$$

If the polarizability of the molecules and ions is supposed isotropic

$$a = \{\alpha, \alpha, \alpha, \dots, \alpha; \alpha_\alpha, \alpha_\beta\} \quad (55)$$

According to the rules of multiplication of matrices, we have

$$\begin{aligned} \frac{1}{2}\mathcal{S}\mathcal{A}\mathcal{S} = \frac{1}{2}q_\alpha^2(\dots) + \frac{1}{2}q_\beta^2(\dots) + q_\alpha q_\beta [\mathbf{s}_{\alpha i} a_i \mathbf{s}_{\beta i} - \\ - \mathbf{s}_{\alpha i} a_i \mathbf{T}_{ij} a_j \mathbf{s}_{\beta j} + \dots - \dots] \end{aligned} \quad (56)$$

where all $i, j, k = 1, 2, \dots, N$, α, β , with the conventions

$$\mathbf{s}_{\alpha\alpha} = \mathbf{s}_{\beta\beta} = 0; \quad \mathbf{T}_{ii} = 0; \quad a_{ii} = a_i \quad (57)$$

The terms are conveniently represented graphically; the open circles represent the ions, the full circles the molecules, and bonds the $\mathbf{s}$ or $\mathbf{T}$ factors. Every term of the expansion (56) is represented by a succession of connected bonds (chain diagrams) going from one ion to another. We shall extract the terms containing polarizabilities of ions and treat them separately; accordingly the first three terms of Eq. (56) are represented as follows:

$$\bigcirc - \bigcirc + \bigcirc - \bullet - \bigcirc + \bigcirc - \bullet - \bullet - \bigcirc + \dots \quad (58)$$

It has been shown by Bellemans¹⁰ that if a is separated into

$$a_0 = \overbrace{\{\alpha, \alpha, \dots, \alpha\}}^N \quad (59)$$

and

$$a' = \overbrace{\{\alpha_\alpha, \alpha_\beta, \dots, \alpha_\epsilon\}}^{N_\alpha} \quad (60)$$

then

$$\mathcal{A} = \mathcal{A}_0 + \mathcal{A}' \quad (61)$$

where

$$\mathcal{A}_0 = \alpha(\mathbf{U} + \alpha\mathbf{T})^{-1} \quad (62)$$

and

$$\mathcal{A}' = [\mathbf{U} + (\mathbf{U} + a_0\mathbf{T})^{-1}a'\mathbf{T}]^{-1}(\mathbf{U} + a_0\mathbf{T})^{-1}a'(\mathbf{U} + \mathbf{T}a_0)^{-1} \quad (63)$$

The corrections due to the polarizabilities of the ions are discussed in Section IV-B; we study here the first term

$$\mathcal{S}\mathcal{A}_0\mathcal{S}$$

The first term in the expansion of W_{ch} in powers of the ionic charges is

$$\lambda_1 = q_\alpha q_\beta R_{\alpha\beta}^{-1} + q_\alpha^2(\cdot \cdot \cdot) + q_\beta^2(\cdot \cdot \cdot) + q_\alpha q_\beta \overline{\sum_i \sum_j \mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\beta j}} \quad (64)$$

The terms in q_α^2 and q_β^2 contribute to $w_1^{(\alpha)}$ and $w_1^{(\beta)}$, and the main contribution to $w_2^{(\alpha\beta)}$, besides the direct Coulomb interaction, is

$$q_\alpha q_\beta \int d\mathbf{r}^N \sum_i \sum_j \mathbf{s}_{\alpha i} \{ \alpha(\mathbf{U} + \alpha \mathbf{T})^{-1} \}_{ij} \mathbf{s}_{\beta j} P(0) \quad (65)$$

This is represented by the series of diagrams (58), where now $i, j, k, \dots = 1, 2, \dots, N$ refer only to molecules. For every power of α , the terms referring to identical groups of molecules can be summed and integrated to make the reduced distribution functions appear. It is necessary, however, to distinguish in terms whether the two indices are equal or not, e.g., between $i = j$ and $i \neq j$. The first few terms are

$$\begin{aligned} q_\alpha q_\beta \alpha \int d\mathbf{r}_1 \eta^{(1)}(1; \alpha, \beta) \mathbf{s}_{\alpha 1} \mathbf{s}_{\beta 1} - q_\alpha q_\beta \alpha^2 \int \int d\mathbf{r}_1 d\mathbf{r}_2 \eta^{(2)}(1, 2; \alpha, \beta) \mathbf{s}_{\alpha 1} \mathbf{T}_{12} \mathbf{s}_{\beta 2} \\ + q_\alpha q_\beta \alpha^3 \int \int \int d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \eta^{(3)}(1, 2, 3; \alpha, \beta) \mathbf{s}_{\alpha 1} \mathbf{T}_{12} \mathbf{T}_{23} \mathbf{s}_{\beta 3} \\ + q_\alpha q_\beta \alpha^3 \int \int d\mathbf{r}_1 d\mathbf{r}_2 \eta^{(2)}(1, 2; \alpha, \beta) \mathbf{s}_{\alpha 1} \mathbf{T}_{12} \mathbf{T}_{21} \mathbf{s}_{\beta 1} + \dots \quad (66) \end{aligned}$$

This can be represented by the series of diagrams (58) plus diagrams obtained by “folding” them in all possible ways, the points α and β not taking part in this folding process. This expansion has to be compared with the statistical-mechanical expression for the macroscopic dielectric constant of the solvent, in terms of $1 - \epsilon^{-1}$. It can be obtained by a rearrangement⁹ of the equations of Mandel and Mazur.⁶ We obtain

$$1 - \epsilon^{-1} = 4\pi n \mathbf{e} \sum (\bar{\mathcal{A}}^{-1} + \frac{8}{3}\pi n \mathbf{U} - \bar{\mathbf{T}})_{ik}^{-1} \mathbf{e} \quad (67)$$

where $\mathbf{e}$ is the unit vector in the direction of the external field and $n = N/V$ is the number density. By expanding Eq. (67)

systematically in powers of the polarizability α , we obtain a series of terms of the form

$$\int \mathbf{e} \mathbf{T}_{ij} \dots \mathbf{T}_{lm} \mathbf{e} G(i, j, \dots, m, \dots, h) d\mathbf{r}^h \quad (68)$$

where a product of k tensors involving h particles is multiplied by a function G of the positions of h molecules. G is a combination of the correlation functions $g^{(2)}, \dots, g^{(h)}$ for the pure solvent, obtained from $P_0(0)$ through $n^{(h)}$. The functions G result from the particular form of Eq. (67), which secures the short-range character of the whole expression, so that every term of the expansion of $1 - \epsilon^{-1}$ in powers of α is shape-independent. No long-range shape-dependent term appears, because the combination of the correlation functions vanishes rapidly if the distance of one of the particles involved from the remaining ones increases. For instance, the term in α^3 is given by

$$4\pi(n\alpha)^3 \left[\left(\frac{8}{3}\pi \right)^2 + V^{-1} \int \mathbf{e} \mathbf{T}_{12} \mathbf{T}_{23} \mathbf{e} G(1, 2, 3) d\mathbf{r}_1 d\mathbf{r}_2 d\mathbf{r}_3 \right. \\ \left. + (Vn)^{-1} \int \mathbf{e} \mathbf{T}_{12} \mathbf{T}_{21} \mathbf{e} g^{(2)}(1, 2) d\mathbf{r}_1 d\mathbf{r}_2 \right] \quad (69)$$

where

$$G(1, 2, 3) = g^{(3)}(1, 2, 3) - g^{(2)}(1, 2)g^{(2)}(2, 3) \quad (70)$$

These expressions, however, apparently bear no resemblance to Eq. (66). To make the comparison possible, the terms in both expansions are brought into exact *one-to-one* correspondence. This can be verified⁹ by rearranging Eq. (66), in every power of α , by adding and subtracting adequately chosen integrals. A more convincing procedure is to make the initial expression (65) have a form similar to Eq. (67). Let us introduce a partial average over $N - 1$ or $N - 2$ coordinates, so that

$$\int d\mathbf{r} N P(0) \sum_i \sum_j \mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\beta j} \equiv N \int d\mathbf{r}_i \mathbf{s}_{\alpha i} \langle \mathbf{A}_{ii} \rangle \mathbf{s}_{\beta i} \\ + N(N - 1) \int \int d\mathbf{r}_i d\mathbf{r}_j \mathbf{s}_{\alpha i} \langle \mathbf{A}_{ij} \rangle \mathbf{s}_{\beta j} \quad (71)$$

If we write $\mathcal{A}$ as

$$\langle \mathbf{A}_{ij} \rangle = (\langle \mathcal{A} \rangle^{-1} + \langle \mathbf{T} \rangle - \langle \mathbf{T} \rangle)_{ij}^{-1} \quad (72)$$

then, when $\langle \mathcal{A} \rangle^{-1}$ and next the whole expression are expanded in powers of α , the terms of the resulting expansion and of the

expansion of (67) are in an exact one-to-one correspondence. The new terms are of two types:

(a) Those containing chain-like products of T-tensors, which would be of a long-range character if there were no **s**-vectors, being in a one-to-one correspondence with the $(\frac{8}{3}\pi)$ terms in the expansion of Eq. (67) and being of the form

$$\alpha^h \int d\mathbf{r}^h \mathbf{s}_{\alpha i} \mathbf{T}_{ij} \gamma^{(2)}(i, j) \mathbf{T}_{jk} \gamma^{(2)}(j, k) \dots \mathbf{T}_{lm} \gamma^{(2)}(l, m) \mathbf{s}_{\beta m} \prod^{(h)} \eta^{(1)}$$

where $\gamma^{(2)}$, the analogue of $g^{(2)}$, is a two-molecule correlation function in the presence of two discharged ions α and β . Similarly, $\eta^{(1)}$ is the analogue of n .

(b) Those terms which would be of a short-range character, each becoming identical with the corresponding term of the expansion of Eq. (67) when two **e**-vectors are substituted for two **s**-vectors and when the reduced distribution functions $n^{(h)}$ are substituted for $\eta^{(h)}$.

Let us introduce the approximation

$$P(0) = P_0(0); \quad \eta^{(h)} = n^{(h)} \quad (73)$$

which means that we treat the ions as point charges. The terms (a) take the form

$$(\alpha n)^h \int d\mathbf{r}^h \mathbf{s}_{\alpha i} \mathbf{T}_{ij} g^{(2)}(i, j) \mathbf{T}_{jk} g^{(2)}(j, k) \dots \mathbf{T}_{lm} g^{(2)}(l, m) \mathbf{s}_{\beta m} \quad (74)$$

It can be shown¹¹ rather easily by convolution theorems that

$$(n\alpha)^h \int d\mathbf{r}^h \mathbf{s}_{\alpha i} \mathbf{T}_{ij} \mathbf{T}_{jk} \dots \mathbf{T}_{lm} \mathbf{s}_{\beta m} = \frac{4\pi n\alpha}{R_{\alpha\beta}} \left(\frac{8\pi n\alpha}{3} \right)^{h-1} \quad (75)$$

This integral gives the correct contribution to the respective terms in $(\epsilon R_{\alpha\beta})^{-1}(\epsilon - 1)q_\alpha q_\beta$. Thus, the possible difference in the values of Eqs. (74) and (75) constitutes a correction to the macroscopic law.

The terms (b) take the form

$$\int d\mathbf{r}^h \mathbf{s}_{\alpha i} F(i, \dots, m, \dots, h) \mathbf{s}_{\beta m} \quad (76)$$

and are in one-to-one correspondence with the terms

$$\int d\mathbf{r}^h \mathbf{e} F(i, \dots, m, \dots, h) \mathbf{e} \quad (77)$$

from Eq. (67). The common function F is a product of $\mathbf{T}$ -tensors multiplied by the appropriate G function. Let us imagine now that integrations have been performed over the coordinates of all the molecules except for those interacting directly with the ions through the $\mathbf{s}$ -vectors or with the homogeneous field through the $\mathbf{e}$ -vectors, i.e., those labelled i and m . Two cases have to be distinguished. First, if $i = m$ a scalar remains after the preliminary integrations, thus

$$C \int d\mathbf{r}_i \mathbf{s}_{\alpha i} \mathbf{U} \mathbf{s}_{\beta i} = C \int \frac{\mathbf{r}_{\alpha i} \mathbf{r}_{\beta i}}{r_{\alpha i}^3 r_{\beta i}^3} d\mathbf{r}_i = C \frac{4\pi}{R_{\alpha\beta}} \quad (78)$$

from Eq. (76), and

$$C 4\pi V^{-1} \int \mathbf{e} \mathbf{U} \mathbf{e} d\mathbf{r}_i = 4\pi C \quad (79)$$

from Eqs. (67) and (77). Therefore, for point ions, these terms give the exact contribution to $w_2^{(\alpha\beta)}$.

In the other instance, $i \neq m$, after the preliminary integrations there remains a tensor G which is a function of the relative distance vector $\mathbf{r}_{im}$. Its most general form is

$$G(\mathbf{r}) = f(r)\mathbf{U} + h(r)(\mathbf{r}\mathbf{r}/r^2) \quad (80)$$

because F was a product of $\mathbf{T}$ -tensors multiplied by a scalar function. The (unknown) functions f and h must fall off rapidly enough with increasing r , as F was of short-range character. Thus we obtain, respectively,

$$\int \mathbf{s}_{\alpha i} G(\mathbf{r}_{im}) \mathbf{s}_{\beta m} d\mathbf{r}_i d\mathbf{r}_m \quad (81)$$

and

$$4\pi V^{-1} \int \mathbf{e} G(\mathbf{r}_{im}) \mathbf{e} d\mathbf{r}_i d\mathbf{r}_m = (4\pi)^2 \int_0^\infty r^2 dr (f + \frac{1}{3}h) \quad (82)$$

The integral (81) has been evaluated⁹ using Fourier transforms with the result

$$\begin{aligned} & \int \mathbf{s}_{\alpha i} G(\mathbf{r}_{im}) \mathbf{s}_{\beta m} d\mathbf{r}_i d\mathbf{r}_m \\ &= R_{\alpha\beta}^{-1} (4\pi)^2 \int_0^{R_{\alpha\beta}} (f + \frac{1}{3}h) r^2 dr + (4\pi)^2 \int_{R_{\alpha\beta}}^\infty r dr [f + \frac{1}{3}h(R/r)^2] \end{aligned} \quad (83)$$

Here the range of validity of the macroscopic expression (1) is clearly shown. Let r^* be the maximum relative distance at which correlations of molecules play any role. The overwhelming contribution to (82) comes from the regions in which $r < r^*$. If $R_{\alpha\beta} \gg r^*$, the expression (83) reduces to the first integral, the second being negligible, and the integrations with the upper limit of $R_{\alpha\beta}$ or infinity give virtually the same result. In such a case, the contributions of the terms (81) and (82) to $w_2^{(\alpha\beta)}$ and to (1) are identical. If, however, $R_{\alpha\beta}$ is comparable to r^* , differences do arise and, therefore, Eq. (1) is no longer valid. As to the long-range terms (a), it can be shown in a similar way that the integrals (74) reduce to (75) if $R_{\alpha\beta} \gg r^*$, where r^* is defined by $g(r) = 1$ for $r > r^*$.

This discussion shows clearly that (1) is an asymptotic formula for macroscopic $R_{\alpha\beta}$ and that "macroscopic" means larger than the distances to which the correlations in positions of molecules extend.

It is interesting to note that even when distribution functions for solvent molecules in the presence of discharged ions are approximated by the distribution functions for the pure liquid solvent and even when the dimensions of the ions are supposed negligible, the fact alone that $R_{\alpha\beta}$ is not infinite on a microscopic scale gives rise to corrections to Eq. (1). These corrections enter through two-particle terms ($i \neq m$).

The next approximation would be to consider charged hard spheres instead of point ions. The first approximation to reduced distribution functions in the presence of two discharged hard spheres is

$$\eta^{(h)} = n^{(h)} \exp [-\beta U_{sh}^{(h)}] \quad (84)$$

The exponential factor

$$\exp [-\beta \sum_i (u_{i\alpha}^{(sh)} + u_{i\beta}^{(sh)})] \quad (85)$$

is zero if any of the h molecules is inside the sphere centered on the ion of radius $\delta = a + b$, where a is the radius of the hard-sphere ion and b is that of the solvent molecule. Its effect is, therefore, to exclude from all the integrals discussed above two spheres of radius δ centered on the ions α and β . Preliminary calculations have shown that the effect of these corrections is

rather small for $R_{\alpha\beta} > 4\delta$. If the volumes of ions are excluded only for the molecules directly connected with the ions by the **s**-bonds, i.e., i or i and m , the integrals (75) and (78) conserve their respective values, and the integral (83) is modified to

$$R_{\alpha\beta}^{-1} \int_0^{R-2\delta} (f + \frac{1}{3}h)r^2 dr + \dots \quad (86)$$

The first term gives an overwhelming contribution for molecules interacting with a potential falling as r^{-6} or faster, if $R_{\alpha\beta}$ is larger than several molecular diameters.

In this way we have shown that the Coulomb macroscopic law (1) can be obtained as an asymptotic approximation to the potential of the average force between two ions in a non-polar solvent.

The next semi-invariant

$$4\lambda_2 = \overline{(\mathcal{P}\mathcal{A}\mathcal{P})(\mathcal{P}\mathcal{A}\mathcal{P})} - \overline{(\mathcal{P}\mathcal{A}\mathcal{P})} \overline{(\mathcal{P}\mathcal{A}\mathcal{P})} \quad (87)$$

gives corrections proportional to the fourth power in the ionic charges: $q_\alpha^4(\dots)$, $q_\beta^4(\dots)$,

$$q_\alpha^3 q_\beta \sum_{i,j,k,l} \overline{(\mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\alpha j})(\mathbf{s}_{\alpha k} \mathbf{A}_{kl} \mathbf{s}_{\beta l})} - \overline{(\mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\alpha j})} \overline{(\mathbf{s}_{\alpha k} \mathbf{A}_{kl} \mathbf{s}_{\beta l})} \quad (88)$$

a symmetrical term in $q_\alpha q_\beta^3$, and two terms in $q_\alpha^2 q_\beta^2$:

$$q_\alpha^2 q_\beta^2 \sum_{i,j,k,l} \overline{(\mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\beta j})(\mathbf{s}_{\alpha k} \mathbf{A}_{kl} \mathbf{s}_{\beta l})} - \overline{(\mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\beta j})} \overline{(\mathbf{s}_{\alpha k} \mathbf{A}_{kl} \mathbf{s}_{\beta l})} \quad (89)$$

and

$$q_\alpha^2 q_\beta^2 \sum_{i,j,k,l} \overline{(\mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\alpha j})(\mathbf{s}_{\beta k} \mathbf{A}_{kl} \mathbf{s}_{\beta l})} - \overline{(\mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\alpha j})} \overline{(\mathbf{s}_{\beta k} \mathbf{A}_{kl} \mathbf{s}_{\beta l})} \quad (90)$$

When $\mathcal{A}$ is expanded in powers of α , and the polarizabilities of the ions are again neglected, only short-range terms appear. For the first term, in α^2 , we find from Eq. (88):

$$\alpha^2 \iint d\mathbf{r}_1 d\mathbf{r}_2 [\eta^{(2)}(1,2) - \eta^{(1)}(1)\eta^{(1)}(2)] r_{\alpha 1}^{-4} \mathbf{s}_{\alpha 2} \mathbf{s}_{\beta 2} \quad (91)$$

The combination of distribution functions ensures a small distance r_{12} between molecules 1 and 2. For large distances, $R_{\alpha\beta}$, the integral (91) can be approximated by

$$\int d\mathbf{r}_2 r_{\alpha 2}^{-4} (\mathbf{s}_{\alpha 2} \cdot \mathbf{s}_{\beta 2}) \quad (92)$$

which can be shown to vary as $R_{\alpha\beta}^{-5}$. Similarly, the first term of (89) can be approximated by a one-particle integral varying as $R_{\alpha\beta}^{-4}\delta^{-1}$, where δ is the radius of the spheres around the ions which are excluded to prevent a short-range divergence.

It may be reasonably concluded that no long-range correction appears which varies more slowly than $R_{\alpha\beta}^{-4}$, in as far, at least, as short-range forces are assumed to operate between the molecules.

For three ions, the irreducible terms contributing to $w_3^{(\alpha\beta\gamma)}$, and varying as $q_\alpha^2 q_\beta q_\gamma$, come out of the second semi-invariant. Because of the lack of a useful approximation to higher distribution functions, even for a pure solvent, we postpone the discussion of these terms for ions in a non-polar solvent.

B. The Rigid-Lattice Model¹¹

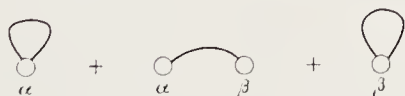
The calculations of the preceding section are greatly simplified if the solvent molecules are assumed to occupy the sites of a regular lattice of high symmetry. The ions are placed in interstitial positions. In this case,¹¹ the first semi-invariant is equal to

$$\frac{1}{2}\mathcal{S}\mathcal{A}\mathcal{S} + \sum_{\alpha < \beta} \frac{q_\alpha q_\beta}{R_{\alpha\beta}}$$

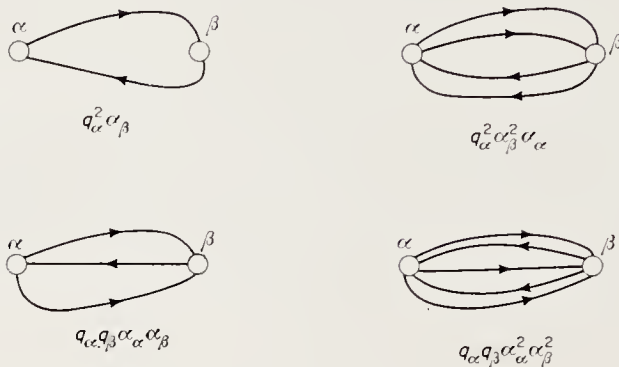
and, when $\mathcal{A}$ is expanded in powers of the polarizabilities, all the terms are summed over the lattice sites and the positions of the ions. All higher semi-invariants vanish. The tensor $\mathcal{A}$ is divided into $\mathcal{A}_0$ and $\mathcal{A}'$; the first term has been studied¹¹ recently. When expanded in a power series of α , it gives multiple independent lattice sums which can be represented by the series of diagrams (58). This succession of chains of T -bonds and s -bonds is represented symbolically as:



The term $\mathcal{S}\mathcal{A}_0\mathcal{S}$ is a sum of three types of diagrams:



and the chains going from one ion to another contribute to $w_2^{(\alpha\beta)}$. The tensor $\mathcal{A}'$, which is related to the polarizabilities of the ions, generates the following successions of chains:¹⁰



and symmetrical terms in q_β^2 . A method for summing a succession of chains by convolution theorems introducing finite Fourier transforms of $\mathbf{s}$ and $\mathbf{T}$ has been described earlier.¹¹ No method, however, exists for a simple estimation of the slowly convergent sums which are obtained. We are left, therefore, to use the continuum approximation, in which the lattice sums are replaced by the corresponding integrals. In this approximation, the Fourier transform of $\mathbf{s}_{\alpha i}$ is

$$\sigma(\mathbf{k}) = \sum_i \mathbf{s}_{\alpha i} e^{i\mathbf{k}\mathbf{r}_{\alpha i}} \simeq a^{-3} \int r^{-3} \mathbf{r} e^{i\mathbf{k}\mathbf{r}} d\mathbf{r} = a^{-3} 4\pi i \mathbf{k} k^{-2} \quad (93)$$

and the Fourier transform of $\mathbf{T}$ is

$$\tau(\mathbf{k}) = \sum_j \mathbf{T}_{ij} e^{i\mathbf{k}\mathbf{r}_{ij}} \simeq a^{-3} \int d\mathbf{r}_{ij} e^{i\mathbf{k}\mathbf{r}_{ij}} \mathbf{T}_{ij} = \frac{4\pi}{a^3} \begin{pmatrix} \frac{2}{3} & 0 & 0 \\ 0 & -\frac{1}{3} & 0 \\ 0 & 0 & -\frac{1}{3} \end{pmatrix} \quad (94)$$

where $\mathbf{k}$ is the Fourier vector. For the $\mathcal{S}\mathcal{A}_0\mathcal{S}$ term the macroscopic approximation (1) is recovered. For the remaining terms rather involved expressions are obtained,¹⁰ the final result is

$$\begin{aligned} \frac{q_\alpha q_\beta}{\varepsilon R_{\alpha\beta}} + \left[1 - \frac{4\alpha_\alpha \alpha_\beta}{\varepsilon^2 R_{\alpha\beta}^6} (\varepsilon B)^4 \right]^{-1} \left[-\frac{q_\alpha^2 \alpha_\beta}{2\varepsilon^2 R_{\alpha\beta}^4} (\varepsilon B)^2 - \frac{q_\beta^2 \alpha_\alpha}{2\varepsilon^2 R_{\alpha\beta}^4} (\varepsilon B)^2 \right. \\ \left. + \frac{2q_\alpha q_\beta \alpha_\alpha \alpha_\beta}{\varepsilon^3 R_{\alpha\beta}^7} (\varepsilon B)^4 \right] \quad (95) \end{aligned}$$

where

$$B \equiv (\epsilon + 2)/3\epsilon = [1 + 8\pi n\alpha_0/3]^{-1} \quad (96)$$

The result can be compared with the macroscopic expression as given by Böttcher,¹² which is of a similar form but with the factor ϵB omitted everywhere. This is an unexpected result, where the macroscopic expression has not been recovered exactly despite the assumptions which were introduced and which gave Eq. (1) exactly when the polarizabilities of the ions were neglected.¹¹ The appearance of the B -factor corresponds to a Lorentz field polarizing the particle: a field $\mathbf{E} = q\epsilon^{-1}\mathbf{s}$ gives rise to a local field

$$\mathbf{E} + \frac{4}{3}\pi\mathbf{P} = \frac{1}{3}(\epsilon + 2)\mathbf{E}$$

and the work $-\frac{1}{2}\alpha E^2$, equal to $-\frac{1}{2}q^2R^{-4}B^2\alpha$ in our case.

A semi-macroscopic calculation of $w_2^{(\alpha\beta)}$ has been described by Levine and Wrigley.¹³ An infinite continuum of given dielectric constant is considered, with two cavities of radius a in which charge distributions are placed. The charge distributions are described by charges, polarizabilities and quadrupole moments, and these quantities are calculated for a model of ions each surrounded by four molecules of water in a chosen configuration. From the usual boundary conditions at the boundary of one cavity and from a cycle involving the transfer of ions from a vacuum to the solvent, w_2 is calculated. The correction to Eq. (1) is shown to vary as $R_{\alpha\beta}^{-4}$ and faster. However, Bellemans' equation (95), when expanded in powers of $R_{\alpha\beta}^{-1}$, is not obtained as a special case of the Levine and Wrigley expression.

V. POTENTIAL OF THE AVERAGE FORCE BETWEEN TWO AND THREE IONS IN A DIPOLAR SOLVENT

A. Asymptotic Coulomb Law for Two Ions

For the model of rigid solvent molecules and ions, U_{ch} is linear in the ionic charges (excluding the direct Coulomb interaction). If the work of charging the ions is expanded in powers of the ionic charges, the first semi-invariant is of the form

$$\frac{q_\alpha q_\beta}{R_{\alpha\beta}} + q_\alpha(\cdot \cdot \cdot) + q_\beta(\cdot \cdot \cdot)$$

The main contribution to w_2 comes from the second semi-invariant and is of the form

$$\lambda_2 = q_\alpha^2 (\dots) + q_\beta^2 (\dots) + q_\alpha q_\beta \overline{\sum_i \sum_j v_{\alpha i} v_{\beta j}} \quad (97)$$

where $v_{\alpha i}$ describes the electrostatic ion-molecule interaction, depending on the distance r_{ij} and the orientation of the molecule. When $v_{\alpha i}$ is expanded, the first term in the expression is the ion-dipole term (cf. Section II), and this term alone gives the macroscopic expression (1) asymptotically. This has been demonstrated¹⁴ for spherical molecules with embedded point dipoles in a very similar way to that described in Section IV-A.

A more general proof would be possible if a systematic way of extracting the long-range dipole-dipole forces was elaborated so as to separate clearly the long-range shape-dependent terms from the short-range terms depending on the orientations of the molecules. In the case of spherical molecules with embedded point dipoles, the separation of the long-range terms is relatively easy, as the division of U_{ch} into long-range and short-range terms coincides with the division into orientation-dependent and orientation-independent terms. In this case, after U_{ch} has been expanded in powers of $\beta\mu^2$ and averages over the orientations of the molecules have been taken, the types of integrals obtained are exactly analogous to those discussed in Section IV-A, so that a parallel reasoning can be used.

B. Rigid-Lattice Model of Solvent Structure

Some calculations have been made^{15,16} for a particularly simple model in which the solvent molecules are located at the sites of a regular lattice. The ions may be placed in interstitial positions or chosen lattice sites. Although this is a very crude approximation, it has the advantage of simplifying the calculations so that these can be carried out far enough. The macroscopic dielectric constant has also been calculated by Rosenberg and Lax¹⁷ for a highly symmetrical lattice of rigid point dipoles. Accordingly, we consider a rigid lattice of point dipoles for which

$$P(0) = \prod_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}_{0i}) \quad (98)$$

where $\mathbf{r}_{0i}$ are the positions of the lattice sites, possibly with the exception of those at which ions are placed. U_{ch} is given by Eqs. (27) and (28), and for two ions the first semi-invariant gives the direct Coulomb interaction, whereas

$$\lambda_2 = q_\alpha q_\beta \overline{s_\alpha s_\beta} \quad (99)$$

where we abbreviate

$$\sum_{i=1}^N \mathbf{s}_{\alpha i} \mathbf{m}_i, \quad \sum_{i=1}^N \mathbf{s}_{\beta i} \mathbf{m}_i \quad (100)$$

by s_α and s_β , respectively. Substituting into (42) and (43) and using Eq. (98) gives

$$\lambda_2 = q_\alpha q_\beta \frac{\int d\boldsymbol{\omega}^N s_\alpha s_\beta e^{-\beta V}}{\int d\boldsymbol{\omega}^N e^{-\beta V}} \quad (101)$$

where

$$V = \sum_{i < j} v_{ij}; \quad v_{ij} = \mathbf{m}_i \mathbf{T}_{ij} \mathbf{m}_j \quad (102)$$

is the dipole-dipole energy. It will also be treated as a perturbation; when expression (100) is expanded systematically in powers of β , the canonical average over orientations of the dipoles is transformed into *a priori* averages

$$\langle X \rangle = \int d\boldsymbol{\omega}^N X / \int d\boldsymbol{\omega}^N \quad (103)$$

The full expansion in powers of β has been discussed elsewhere¹⁴ (cf. also Mandel and Mazur⁶); e.g., the term in β^3 is:

$$\langle s_\alpha s_\beta V^2 \rangle - \langle s_\alpha s_\beta \rangle \langle V^2 \rangle \quad (104)$$

(remembering that $\langle V \rangle = 0$). The average over a group of specified dipoles factorizes into a product of independent averages; the average over the orientations of one dipole can be computed according to well-known rules; if the dipole $\mathbf{m}_i$ is multiplied by vectors $\mathbf{e}_1, \mathbf{e}_2, \dots$, then

$$\begin{aligned} (\mathbf{m}_i \mathbf{e}_1)(\mathbf{m}_i \mathbf{e}_2) &= \frac{1}{3} \mu^2 (\mathbf{e}_1 \mathbf{e}_2); \\ (\mathbf{m}_i \mathbf{e}_1)(\mathbf{m}_i \mathbf{e}_2)(\mathbf{m}_i \mathbf{e}_3)(\mathbf{m}_i \mathbf{e}_4) &= \\ \frac{1}{15} \mu^4 [(\mathbf{e}_1 \mathbf{e}_2)(\mathbf{e}_3 \mathbf{e}_4) + (\mathbf{e}_1 \mathbf{e}_3)(\mathbf{e}_2 \mathbf{e}_4) + (\mathbf{e}_1 \mathbf{e}_4)(\mathbf{e}_2 \mathbf{e}_3)] \end{aligned} \quad (105)$$

and

$$\sum_{r=1}^k (\mathbf{m}_i \mathbf{e}_r) = 0 \quad \text{for } k \text{ odd} \quad (106)$$

Therefore each term of the initial form

$$s_\alpha s_\beta V^n$$

generates a multitude of terms, according to whether the indices of summations over the lattice sites are equal or not. It is convenient to represent the terms graphically. We use the same

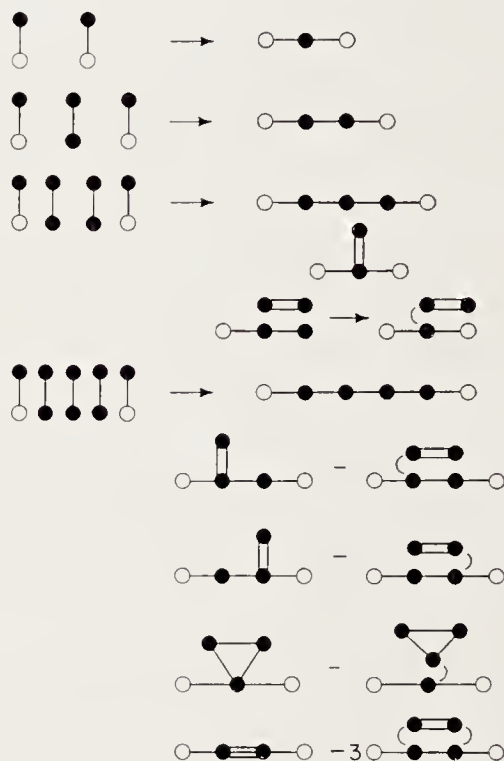


Fig. 1. Construction of the first few diagrams in $q_\alpha q_\beta$ for two ions.

convention as before, where two open circles denote the ions and full circles the molecules. The first few diagrams are assembled in Fig. 1—the first is zero on averaging because of (106), unless $i = j$, which is the case for the second diagram. In general, the initial two s -bonds and n T -bonds have to be connected to form a diagram in which an even number of bonds meets at any point representing a dipole. Next, the terms represented by diagrams having totally disconnected parts are destroyed by similar terms of sums such as (104); there remain residual terms which contain the same type of lattice sums as a connected diagram and which

are accordingly combined with such. This is so in the case of the third diagram with two T -bonds; the remaining term is combined with the second diagram and the two points which have to be identified *after* averaging over orientations are indicated by a small arc. We therefore have to take into account the connected diagrams with an even number of bonds meeting at each point, each connected diagram being in fact composed of the main diagram and its decompositions into partial averages (arc-containing diagrams).

In the final stage, the diagrams are converted into multiple independent lattice sums by adding and subtracting the terms in which two or more points are identified (i.e., the corresponding expression is multiplied by a Kronecker delta factor); this procedure generates more compact decomposed diagrams, which are again combined with the corresponding lattice sums. The first diagram in β^3 , for instance, gives a triple independent lattice sum plus a term

$$(\frac{1}{3}\mu^2)^3 \mathbf{s}_{\alpha i} \mathbf{T}_{ij} \mathbf{T}_{ji} \mathbf{s}_{\beta i} \quad (107)$$

which is combined with the second diagram in β^3 .

It is not difficult to draw all the diagrams of a given power of β , since they are all obtained by folding an Eulerian chain of given lengths going from one ion to the other. We observe that for every power of β , the largest possible number of lattice points is involved in the simple-chain diagram; also, once a given pattern of bonds has appeared for some power of β , it will obviously be repeated indefinitely as T -bonds are added successively on α - and β -sides. Accordingly, it is useful to classify the diagrams into (a) simple chain, (b) simple chain with attached "compact fragment", and (c) simple chain with "built in" compact fragments. A set containing identical compact fragments has been called a family of diagrams. The first few families are shown in Fig. 2; they are simple chains and simple chains containing what has been called $\mathfrak{R}$, $\mathfrak{I}$, and $\mathfrak{S}$ compact fragments.

It is not difficult to evaluate the contributions of "attached fragments" like $\mathfrak{R}$. For any given configuration of the remaining points of a diagram, we can perform the summation over the $n - 1$ points of the given fragment and the result is a scalar for a

lattice of sufficiently high symmetry. It has been shown that every $\mathfrak{R}$ fragment gives a contribution

$$(n\gamma)^2 \mathfrak{R} = 2 \sum_j r_{ij}^{-6} (n\gamma)^2 \quad (108)$$

where

$$n\gamma = N\mu^2/3VkT \quad (109)$$

which simply multiplies the contribution of the remaining diagram without that $\mathfrak{R}$ fragment.

The simple chains can be summed by applying the convolution theorems [cf. Section IV-B and Eq. (75)]. As no method exists

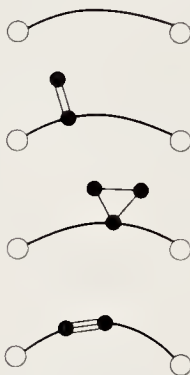


Fig. 2. The first few families of diagrams in $q_\alpha q_\beta$ for two ions.

for calculating the lattice sums needed, we introduce the continuum approximation, in which the lattice sums are replaced by the corresponding integrals. In this approximation, the diagrams can be successively reduced because every T -bond gives a contribution equal to $\frac{8}{3}\pi$. In fact, we have

$$\int d\mathbf{r}_j \mathbf{T}_{ij} \mathbf{T}_{jk} = \frac{8}{3}\pi \mathbf{T}_{ik} \quad (110)$$

Also

$$\int d\mathbf{r}_i \mathbf{s}_{\alpha i} \mathbf{T}_{ij} = \frac{8}{3}\pi \mathbf{s}_{\alpha j} \quad (111)$$

and

$$\int d\mathbf{r}_i \mathbf{s}_{\alpha i} \mathbf{s}_{\beta i} = 4\pi R_{\alpha\beta}^{-1} \quad (112)$$

Since there is one chain diagram for every power of β , which therefore gives the contribution

$$4\pi n\gamma \left(-\frac{8}{3}\pi n\gamma\right)^k \quad (113)$$

the contribution of the whole family of simple chains is

$$q_\alpha q_\beta 4\pi n\gamma [1 + \frac{8}{3}\pi n\gamma]^{-1} \quad (114)$$

This is the correct contribution to $(\epsilon R_{\alpha\beta})^{-1}(\epsilon - 1)$ if the macroscopic dielectric constant is given by the Debye approximation:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n\gamma \quad (115)$$

If all the diagrams containing one, two, . . . , etc. $\mathfrak{R}$ fragments¹⁵ are enumerated, the result is again in accordance with the macroscopic Coulomb law if ϵ is given by the van Vleck expression:

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n\gamma [1 - \mathfrak{R}(n\gamma)^2] \quad (116)$$

Preliminary calculations have shown that the inclusion of all families containing $\mathfrak{I}$ and $\mathfrak{S}$ fragments together with mixed terms does not change this result significantly, and the agreement is maintained if we use the Rosenberg and Lax¹⁷ expression for ϵ

$$\frac{\epsilon - 1}{\epsilon + 2} = \frac{4}{3}\pi n\gamma [1 - \mathfrak{R}(\gamma n)^2 + (-\mathfrak{I} + \frac{4}{5}\mathfrak{S})(n\gamma)^3] \quad (117)$$

The macroscopic Coulomb law is therefore recovered under the approximation of replacing the long-range lattice sums in chain-like parts of diagrams by the corresponding integrals multiplied by the average density n . The lattice sums in compact fragments are not replaced by the integrals. The first source of possible corrections is thus in the long-range lattice sums. Also, there is an important difference between compact fragments of diagrams which are attached to a chain and those which are built in, for the lattice sum over one point of an $\mathfrak{R}$ fragment can be performed freely, whereas a change in position of one point of an $\mathfrak{S}$ fragment affects the configuration of the neighbouring T -bonds. For this reason, in the case of ϵ being given by (117), the agreement with the macroscopic law was only approximate. This is similar to the difference between A_{ii} and A_{im} discussed in Section IV.

C. Higher Powers of Ionic Charges

Similar calculations can be repeated for higher semi-invariants. For our simple model of point dipoles and spherical ions, the third semi-invariant gives zero contribution to $w_2^{(\alpha\beta)}$, and the fourth

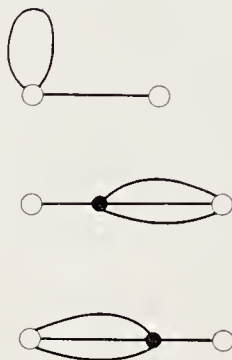


Fig. 3. The first few families of diagrams in $q_\alpha^3 q_\beta$ and $q_\alpha q_\beta^3$ for two ions.

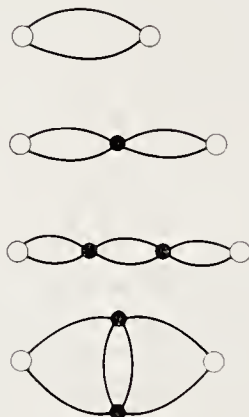


Fig. 4. The first few families of diagrams in $q_\alpha^2 q_\beta^2$ for two ions.

gives three terms proportional to $q_\alpha q_\beta^3$, $q_\alpha^2 q_\beta^2$, and $q_\alpha^3 q_\beta$, respectively. Since the first moment vanishes by symmetry, we have

$$\lambda_4 = m_4 - 3m_2^2 \quad (118)$$

and this, when expanded in powers of β , generates the diagrams whose first few families are assembled in Figs. 3 and 4. The important difference from the diagrams discussed above is that

we dispose now of four $\mathbf{s}$ -bonds which can therefore give four simple chains. Diagrams with totally independent chains are destroyed by their decompositions generated by the $-3m^2$ term of (118). First the diagrams with one knotted point (sometimes called a bridge-point or a nodal-point) appear, then the diagrams with two knotted points, etc. To these simple chains can be attached all the compact fragments found previously when calculating λ_2 . The diagrams of the first family with one knotted point have been enumerated;¹⁶ for the n th power of β there are

$$n! \binom{4+n-1}{n} \quad (119)$$

diagrams, corresponding to the number of ways of distributing n T -bonds between four ordered cells. Introducing the continuum approximation, i.e., replacing lattice sums by integrals, one finds the following contribution:¹⁵

$$\begin{aligned} & -\frac{1}{10}q_\alpha^2q_\beta^2\beta B^4\gamma^2\sum_i[(\mathbf{s}_{\alpha i}\mathbf{s}_{\alpha i})(\mathbf{s}_{\beta i}\mathbf{s}_{\beta i}) + 2(\mathbf{s}_{\alpha i}\mathbf{s}_{\beta i})^2] \\ & + \frac{1}{5}q_\alpha^3q_\beta\beta B^4\gamma^2\sum_i(\mathbf{s}_{\alpha i}\mathbf{s}_{\alpha i})(\mathbf{s}_{\alpha i}\mathbf{s}_{\beta i}) \\ & + \frac{1}{5}q_\alpha q_\beta^3\beta B^4\gamma^2\sum_i(\mathbf{s}_{\alpha i}\mathbf{s}_{\beta i})(\mathbf{s}_{\beta i}\mathbf{s}_{\beta i}) \end{aligned} \quad (120)$$

The factor B is identical with the one defined in Eq. (96) and results from the sum

$$\sum_{n=0}^{\infty} \left(-\frac{8\pi N\gamma}{3V} \right)^n \frac{(3+n)!}{3!n!} = \left[1 + \frac{8\pi N\gamma}{3V} \right]^{-4} \quad (121)$$

If the lattice sum resulting from the first diagram to which the whole family can be successively reduced is again replaced by the corresponding integral, one obtains:^{16*}

$$\begin{aligned} & \frac{4}{3}\pi R_{\alpha\beta}^{-4}\delta^{-1}q_\alpha^2q_\beta^2\beta\gamma^2nB^4 + O(R_{\alpha\beta}^{-6}) \\ & + \frac{4}{25}\pi R_{\alpha\beta}^{-5}(q_\alpha^3q_\beta + q_\alpha q_\beta^3)\beta\gamma^2nB^4 + O(R^{-7}) \end{aligned} \quad (122)$$

Around each ion a small sphere of radius δ has to be excluded to prevent a short-range divergence.

* Recently [*J. Chem. Phys.* (1963)] D. Jepsen and H. L. Friedman have rederived this result.

The simple form of (122) and the expression for B in terms of ϵ are maintained if $\Re$ compact fragments are accounted for. The numerical value of the correction would be modified if more complicated families of diagrams were taken into account; nevertheless, all terms are of dimension (length) $^{-5}$ and vary as $R_{\alpha\beta}^{-4}$ or faster.

D. Irreducible Interactions between Three Ions, $w_3^{(\alpha\beta\gamma)}$

In our model, λ_2 does not contribute to $w_3^{(\alpha\beta\gamma)}$; from λ_4 three symmetrical terms result, proportional to $q_\alpha^2 q_\beta q_\gamma$, $q_\alpha q_\beta^2 q_\gamma$, and $q_\alpha q_\beta q_\gamma^2$. When developing λ_4 in powers of β , diagrams with one knotted point bound to the ions through simple chains appear first. This family can be easily summed by the methods outlined above, again leading to the factor B^4 multiplying the first diagram. The lattice sum corresponding to the first diagram leads, however, to three-centre integrals, like:

$$\int dr_i \frac{\cos(\beta, \gamma) + 2 \cos(\alpha, \beta) \cos(\alpha, \gamma)}{r_{\alpha i}^4 r_{\beta i}^2 r_{\gamma i}^2} \quad (123)$$

which has to be evaluated for specified configurations of the three ions α , β , and γ . Here $\cos(\beta, \gamma)$ stands for $\mathbf{r}_{\beta i} \mathbf{r}_{\gamma i} / r_{\beta i} r_{\gamma i}$.

VI. FREE ENERGY OF CHARGING A SINGLE ION

The first attempt to estimate the free energy of hydration of an ion was that of Born, who in 1920 derived from macroscopic electrostatics the following expression

$$w_1^{(\alpha)} = \frac{q_\alpha^2}{2a} \left(1 - \frac{1}{\epsilon} \right) \quad (124)$$

for the work of charging a conducting sphere of radius a imbedded in a medium of macroscopic dielectric constant ϵ . This equation has been extensively used, discussed, and improved. Excellent accounts of various attempts and results, as well as qualitative discussion of the ion-solvent interactions can be found elsewhere.^{18,19,20} Two important features have to be noted. First, only the free energies of solvation *of salts* are derivable from

experimental data, and the division into the contributions of separate ions is always to some extent arbitrary. In general, two or three significant figures at most can be given, and the results of different authors differ by 10 kcal/g. ion or even more. This should be borne in mind when the agreement with experiment of empirical or semi-empirical correlations or equations is considered. Secondly, one conclusion is quite certain; it is that Eq. (124) gives too high values when applied to salts and when a is taken as the crystallographic radius of the ion.

A variety of phenomena can take place, from definite complexes being formed through all possible intermediate situations to purely "physical" interactions acting exclusively. In what follows, the discussion is limited to particularly simple cases, the formation of new chemical species not being considered. We want to show first how Born's equation can be obtained from our expressions for the work of charging an ion.

A. Non-polar Solvents

The model is identical with that discussed in Section IV-A; we consider a spherical ion of charge q_α in a medium of spherical particles of polarizability α . It can be shown that the direct contribution of the polarizability of the ion vanishes owing to the spherical symmetry of the problem.¹⁰ We have

$$-\beta w_1^{(\alpha)} = \ln \int P(0) \exp(-\beta U_{\text{ch}}) d\mathbf{r}^N \quad (125)$$

where

$$U_{\text{ch}} = \frac{1}{2} q_\alpha^2 \sum_i \sum_j \mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\alpha j} \quad (126)$$

The first semi-invariant obtained from (125), expanded in powers of βq_α^2 , is

$$\lambda_1 = \overline{U_{\text{ch}}} = \frac{1}{2} q_\alpha^2 \int P(0) \sum_i \sum_j \mathbf{s}_{\alpha i} \mathbf{A}_{ij} \mathbf{s}_{\alpha j} d\mathbf{r}^N \quad (127)$$

When Eq. (127) is expanded in powers of α , the terms are the exact counterparts of the terms obtained by expanding (65), one $\mathbf{s}_{\alpha j}$ replacing here $\mathbf{s}_{\beta j}$. Therefore the expansion (127) can also be brought into a one-to-one correspondence with the terms resulting from the expansion of $1 - \epsilon^{-1}$. The classification of terms is similar and we have three types of terms:

(a) the chain-like products of T -tensors [cf. Eq. (74)], now connecting the ion to itself,

(b) the terms representing average interaction of the ion with one molecule also polarized by the other $h - 1$ molecules, thus

$$\int d\mathbf{r}^h \mathbf{s}_{\alpha i} F(i, \dots, k, \dots, i) \mathbf{s}_{\alpha i} \eta^{(h)}(\mathbf{r}^h; \mathbf{r}_{\alpha}) \quad (128)$$

(c) the terms representing the average interaction of the ion with two molecules also polarized by the other $h - 2$ molecules, thus

$$\int d\mathbf{r}^h \mathbf{s}_{\alpha i} F(i, \dots, k, \dots, m) \mathbf{s}_{\alpha m} \eta^{(h)}(\mathbf{r}^h; \mathbf{r}_{\alpha}) \quad (129)$$

Clearly $P(0)$ and the functions $\eta^{(h)}$ derived therefrom differ from the corresponding quantities in the pure solvent because of the short-range dispersion and repulsion forces acting between a discharged ion and the solvent molecules. For instance, $n^{(1)} = n = N/V$ is a constant, whereas $\eta^{(1)}$ is similar to $ng^{(2)}$, being a conditional probability of finding a solvent molecule at a given point $\mathbf{r}$ if the discharged ion is at $\mathbf{r}_{\alpha}$. Thus, $\eta^{(1)}$ is zero for very small values of $\mathbf{r}_{\alpha 1}$; it then passes through its first maximum (not far from the distance at which $u_{\alpha i}^{\text{sh}}$ is a minimum) and oscillates about $n(\mathbf{r}) = n$. Therefore, in the immediate vicinity of the ion we cannot expect even an approximate equality of the integrand functions $F\eta^{(h)}$ and $Fn^{(h)}$.

In order to approach Born's approximation more closely, let us consider the hard-sphere interaction between the ion and solvent molecules:

$$u_{\alpha i}^{\text{sh}} = \begin{cases} 0 & r_{\alpha i} \geq \delta \\ \infty & r_{\alpha i} < \delta \end{cases} \quad (130)$$

where δ is the distance of closest approach for an ion-molecule pair

$$\delta = a + b \quad (131)$$

where a is the radius of the ion and b that of the solvent molecule. To a first approximation, we have⁸

$$\eta^{(h)}(r^h) = n^{(h)}(r^h) \prod_{i=1}^h \exp(-\beta u_{i\alpha}) \quad (132)$$

The effect of the exponential factor is to make the volume of the ion inaccessible to solvent molecules, i.e., to exclude a sphere of radius δ centred on the ion from all h three-dimensional integrations, initially extended to the whole volume V . This results from the fact that the interactions are functions of *relative* distances measured from the centres of the particles involved. The effect of *volume exclusion* can be dealt with in a systematic way by introducing the Mayer functions

$$1 + f_{\alpha j} = \exp(-\beta u_{\alpha j}^{\text{sh}}); \quad f_{\alpha j} = \begin{cases} 0 & r_{\alpha j} \geq \delta \\ -1 & r_{\alpha j} < \delta \end{cases} \quad (133)$$

except for the particle, or two particles, directly connected to the ion by two $\mathbf{s}$ -vectors ($j \neq i, j \neq m$). When the product is multiplied out, we obtain a series of terms in which successively $r = 0, 1, \dots, h-1$ (or $h-2$) particles are confined to the sphere of radius δ . The first term ($r = 0$) of every term (a) is

$$(n\alpha)^{h+1} \int_{r_{\alpha i} > \delta} d\mathbf{r}_i \int_{r_{\alpha m} > \delta} d\mathbf{r}_m \int d\mathbf{r}^{h-2} \mathbf{s}_{\alpha i} \mathbf{T}_{ij} g^{(2)}(i, j) \dots \mathbf{T}_{lm} g^{(2)}(l, m) \mathbf{s}_{\alpha m} \quad (134)$$

We note that a similar integral of chain-like products of h tensors without correlation functions is^{11,21}

$$(n\alpha)^{h+1} \int_{r_{\alpha i} \geq \delta} d\mathbf{r}_i \int_{r_{\alpha m} \geq \delta} d\mathbf{r}_m d\mathbf{r}^{h-2} \mathbf{s}_{\alpha i} \mathbf{T}_{ij} \mathbf{T}_{jk} \dots \mathbf{T}_{lm} \mathbf{s}_{\alpha m} = 4\pi n\alpha (8\pi n\alpha/3)^h \delta^{-1} \quad (135)$$

and this would be a correct contribution to $q_\alpha^2(1 - \varepsilon^{-1})/2\delta$. Similarly, the term with $r = 0$ generated by every term of type (b) can be simplified by the arguments used in deriving Eq. (78), and we obtain

$$C \int_{r_{\alpha i} \geq \delta} \mathbf{s}_{\alpha i} \mathbf{s}_{\alpha i} d\mathbf{r}_i = 4\pi C/\delta \quad (136)$$

where C is the scalar resulting from the integration over $h-1$ positions. This is exactly the correct contribution to $q_\alpha^2(1 - \varepsilon^{-1})/2\delta$. Finally, the term with $r = 0$ resulting from a term

of the type (c) can be represented in a form similar to (81), by the same arguments, and integrated to give:

$$\begin{aligned} & \int \int_{\substack{r_{\alpha i} \geq \delta \\ r_{\alpha m} \geq \delta}} d\mathbf{r}_i d\mathbf{r}_m \mathbf{s}_{\alpha i} G(\mathbf{r}_{im}) \mathbf{s}_{\alpha m} \\ &= \frac{(4\pi)^2}{\delta} \int_0^{2\delta} r^2 dr \left[\left(f + \frac{1}{3}h \right) - \frac{r}{4\delta} \left(f + \frac{1}{2}h \right) \right] + (4\pi)^2 \int_{2\delta}^{\infty} r dr \left[f + \frac{2}{3}h \frac{\delta^2}{r^2} \right] \end{aligned} \quad (137)$$

The corresponding contribution to $q_\alpha^2(1 - \varepsilon^{-1})/2$ would be [cf. Eq. (82)]:

$$\frac{(4\pi)^2}{\delta} \int_0^{\infty} r^2 dr \left(f + \frac{1}{3}h \right) \quad (138)$$

What can be shown, therefore, is that some terms can be grouped together to give the expression

$$\frac{q_\alpha^2}{2\delta} \left(1 - \frac{1}{\varepsilon} \right) \quad (139)$$

The remaining terms are the differences between Eqs. (134) and (135), those between (133) and (134), and the volume exclusion corrections to all terms ($r = 1, 2, \dots, h-2$ or $h-1$). No explicit calculations have been attempted, since the distribution functions are not known. The following points are, however, clear:

(i) The volume exclusion terms are corrections; some terms can be shown to vanish and, in general, the numerical values are smaller than those of the corresponding main terms ($r = 0$) on account of the fact that here the particles are confined to a sphere of radius δ whereas in the main term they take all positions in the infinite space.

(ii) It is well known that Eq. (124) gives too high values when compared with experimental free energies of solvation of salts. On the other hand, (139) underestimates $w_1^{(\alpha)}$. Not only were specific interactions not included in our model, but also the distribution functions for the hard-sphere model do not take into account the attraction of molecules to the discharged ion, which

results in a higher probability of finding a molecule near the ion; for example $\eta^{(1)} > n^{(1)}$ for r slightly larger than δ , and the value of the contribution given by Eq. (136) is too low.

(iii) The important point is that the quantity a in Eq. (124) can never have the meaning of the crystallographic radius of the ion. In the hard-sphere model it has to be replaced by δ . In the macroscopic limit $\delta = a + b \simeq a$, Eq. (124) is recovered.²¹

For a non-polar solvent only even powers of q_α contribute to $w_1^{(x)}$. Inspection shows that only short-range terms are involved in powers higher than 2; this is directly due to the assumptions that only a dipole moment is induced and that α is a constant. The very first term in q_α^4 gives $(\mathbf{s}_{\alpha i} \mathbf{s}_{\alpha i})^2 \sim r_{\alpha i}^{-8}$, yielding δ^{-5} on integration. In general, the contributions proportional to higher powers of the ionic charge originate in the immediate neighbourhood of the ion.

B. Polar Solvents

Any explicit calculation is of prohibitive difficulty here. For a model of non-deformable molecules, we find (cf. Sections II-C and III-C)

$$\lambda_1 = q_\alpha \int \rho^{(1)} v_{\alpha 1}(r_{\alpha 1}, \boldsymbol{\omega}_1) d\mathbf{r}_1 d\boldsymbol{\omega}_1 \quad (140)$$

If $\rho^{(1)}$, the one-particle distribution function in the presence of a discharged ion, is not independent of the orientation $\boldsymbol{\omega}_1$, $\lambda_1 \neq 0$. In the immediate neighbourhood of the ion and for molecules of complicated shape (e.g., molecules of water), some contribution proportional to the ionic charge can be expected to arise.

The second semi-invariant is

$$\lambda_2 = q_\alpha^2 \int \rho^{(1)} v_{\alpha 1}^2 d\mathbf{r}_1 d\boldsymbol{\omega}_1 + q_\alpha^2 \iint v_{\alpha 1} v_{\alpha 2} [\rho^{(2)} - \rho^{(1)}(1)\rho^{(1)}(2)] d\mathbf{r}_1 d\boldsymbol{\omega}_1 d\mathbf{r}_2 d\boldsymbol{\omega}_2 \quad (141)$$

and the two-particle distribution function $\rho^{(2)}$ is of long range and depends on the shape of the specimen because of dipole-dipole forces. Similarly, λ_3 involves three particles and $\rho^{(3)}$, λ_4 four particles and $\rho^{(4)}$, etc.

Born's equation is derived from the expression for the free energy of polarization of the solvent, ΔF :

$$4\pi \Delta F = \int_{(\infty)}^D d\mathbf{r} \int_0^D \mathbf{E} \delta \mathbf{D} - \frac{1}{2} \int_{(\infty)} d\mathbf{r} \mathbf{E}_0 \mathbf{D}_0 \quad (142)$$

transformed into

$$\Delta F = \frac{1}{8\pi} \int_{(V)} d\mathbf{r} (\mathbf{E} - \mathbf{D}) \mathbf{D}_0 = -\frac{1}{2} \int_{(V)} \mathbf{P} \mathbf{D}_0 d\mathbf{r} \quad (143)$$

with integrations over the volume of the dielectric. With the substitutions:

$$E_0 = D_0 = q_\alpha |\mathbf{r} - \mathbf{r}_\alpha|^{-2} \quad (144)$$

$$D = D_0 \quad (145)$$

$$4\pi \mathbf{P}(\mathbf{r}) = (\varepsilon - 1) \mathbf{E}(\mathbf{r}) = (\varepsilon - 1) \varepsilon^{-1} \mathbf{D}(\mathbf{r}) \quad (146)$$

$$\varepsilon = \text{const.} \quad (147)$$

Eq. (124) is obtained when a sphere of radius a is excluded from the volume of the dielectric.

Now

$$\mathbf{P}(\mathbf{r}) = \overline{(\sum_i \mathbf{m}_i \delta(\mathbf{r}_i - \mathbf{r}))} (E) \quad (148)$$

where the average is taken in the presence of the field.

If only the interaction between the field and permanent dipoles is taken into account (which is strictly valid only for homogeneous external fields), the distribution function can be expressed as

$$f_N(E) = f_N(0) (1 + \beta \sum_j \mathbf{m}_j \mathbf{E}_0(\mathbf{r}_j) + \dots)$$

and this leads to

$$\mathbf{P}(\mathbf{r}) = \beta \overline{[\sum_i \sum_j \mathbf{m}_i \delta(\mathbf{r}_i - \mathbf{r}) \cdot \mathbf{m}_j \mathbf{E}_0(\mathbf{r}_j)]} \quad (149)$$

Clearly Eq. (146) corresponds to

$$\mathbf{P}(\mathbf{r}) = \beta \overline{[\sum_i \sum_j \delta(\mathbf{r}_i - \mathbf{r}) \mathbf{m}_i \mathbf{m}_j]} \mathbf{E}_0(\mathbf{r}) \equiv \beta \overline{(\mathbf{m} \mathbf{m})} \mathbf{E}_0(\mathbf{r}) \quad (150)$$

which is different from Eq. (149).

From the derivation of Born's equation it is rather clear that the result corresponds to the average ion-dipole interaction. This goes back to the definition of dielectric displacement

$$\mathbf{D} = \mathbf{E} + 4\pi\mathbf{P} \quad (151)$$

where only the dipole moment of the specimen is taken into account. In fact, inserting Eq. (148) into Eq. (143), we obtain

$$\Delta F = -\frac{1}{2} \overline{\sum_i \mathbf{E}_0(\mathbf{r}_i) \mathbf{m}_i} (E) \quad (152)$$

and $\mathbf{E}_0(\mathbf{r}_i) \mathbf{m}_i$ is nothing other than $\mathbf{s}_{\alpha i} \mathbf{m}_i$.

The use of Eq. (150) instead of (149) introduces a further limitation; inserting (150) into (143) and using (144)–(147), we obtain

$$\Delta F = -\frac{1}{2} \int d\mathbf{r} \mathbf{E}_0(\mathbf{r}) \beta \overline{\mathbf{m} \mathbf{m}} \mathbf{E}_0(\mathbf{r}) \quad (153)$$

Of course, all the averages depend on the shape of the dielectric specimen.

Expression (141) contains ion-molecule electrostatic interactions $v_{\alpha i}$ of which the ion-dipole interaction is only the first term. The averaging is also different [compare Eqs. (149) and (150)]; there is, however, no difference in one-particle terms ($i = j$).

With these remarks we leave this discussion. We describe below some explicit calculations which have been performed for a very simple model of a dipolar solvent.

C. Rigid Lattice of Point Non-polarizable Dipoles

We apply the model used in Section IV-B to the case of a single ion. The free energy of charging, $w_1^{(x)}$, is expanded in powers of the ionic charge, q_α , to give a series of Thiele semi-invariants, λ_l , and then every semi-invariant is expanded in powers of $(-\beta V)$ to generate the *a priori* averages over the orientations of the dipoles; this procedure finally yields for $\beta w_1^{(x)}$ a perturbation series in $n\gamma = \frac{1}{3}\beta\mu^2 N/V$ and in $\Gamma_a = \beta q^2 a^{-1}$, where a is the lattice distance. Each term is represented graphically; the diagrams are easily obtained from those discussed for

two ions by putting the point “ β ” on the point representing the ion “ α ”. We classify the diagrams according to:

- (i) the number of s -bonds, which is even and equal to the power of $\Gamma_a^{\frac{1}{2}}$,
- (ii) the number of T -bonds, which is equal to the power of $n\gamma$;
- (iii) the topological structure of the diagrams; we distinguish chain-like parts and compact fragments and we group into families

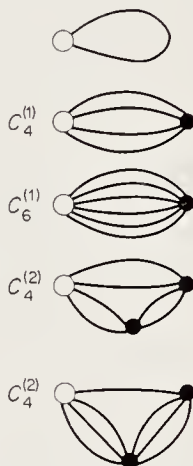


Fig. 5. The families of diagrams for one ion.

the diagrams containing the same compact fragments and the same number and type of knotted points. The first few families of diagrams are shown in Fig. 5. As numerical coefficients of the powers of $n\gamma$ and Γ_a , there appear lattice sums of increasing complexity; as it stands, the problem would be intractable. We therefore introduce the approximation used previously, namely we replace the summations by integrations for all chain-like parts of diagrams and we retain the lattice-summation procedure for all compact fragments and diagrams containing no simple chains. Each T -bond then gives the contribution $\frac{8}{3}\pi$, and any family of diagrams can be successively reduced up to a point where further reduction is no longer possible; the resulting compact diagram with no simple chains of T -bonds is called the prototype of the given family. Conversely, any diagram which is compact, i.e., does not contain chains of single T -bonds, is a prototype of its characteristic family of diagrams which are obtained by inserting successively T -bonds wherever it is possible without violating the

general rules of construction of diagrams.

Let us compare the relative contributions of different families, disregarding for the present purpose the compact fragments, which can be freely attached to chains at all points. For any given power of β , more compact diagrams containing multiple bonds and knotted points are obtained by "folding" less compact ones containing a smaller number of knotted points. Thus, the lattice sum corresponding to a more compact diagram is only a single term of the lattice sum corresponding to the less compact one. Therefore, we should expect that the most important contributions are those of diagrams containing the largest possible number of single bonds or the smallest possible number of knotted points. Explicit calculations for $C_4^{(1)}$ and $C_4^{(2)}$ illustrate the validity of this argument.

The second important point is the question of convergence. As noted, we obtain a perturbation series in $n\gamma$ and in $\Gamma_a = \beta q^2 a^{-1}$. The lattice distance a appears when the lattice sums are converted into non-dimensional ones by introducing r_{ij}/a . In the case of the potential of the average force, the role of Γ_a was played by $\Gamma_R = \beta q^2 R^{-1}$, which could be made arbitrarily small. For a univalent ion at 300°K, $\Gamma_a = 556.9/a$, where a is in Ångstrom units. If we were to use a continuum approximation with a hard-sphere ion-solvent short-range interaction, the parameter would be $\Gamma_\delta = \beta q^2 \delta^{-1}$; this is still a large quantity unless the ion is really large. The parameters found in the expansion are in fact smaller, because combinations of the type $\Gamma_a n\gamma$ or $\Gamma_\delta \delta^{-3}\gamma$ appear rather than Γ_a or Γ_δ alone; nevertheless, the perturbation series is divergent at liquid densities for ions of radius comparable to that of the solvent molecules. Therefore, we have to sum the perturbation series up to an infinite order of Γ . This has been done for the $C_l^{(1)}$ families of diagrams.

For the contribution of a $C_l^{(1)}$ family one obtains

$$P_2 \times \sum_{n=0}^{\infty} \frac{1}{n!} n! (-\frac{8}{3}\pi n\gamma)^n = -\frac{1}{2}\Gamma_a n\gamma (1 + \frac{8}{3}\pi n\gamma)^{-1} S_0 \quad (l=2) \quad (154)$$

$$P_l \times \sum_{n=0}^{\infty} \frac{1}{n!} n! \left(\frac{n+l-1}{n} \right) (-\frac{8}{3}\pi n\gamma)^{-n} = P_l (1 + \frac{8}{3}\pi n\gamma)^{-l} \quad (l \geq 4) \quad (155)$$

where the combinatorial factor is that of distributing n T -bonds in l ordered cells with no restriction as to the number of objects in each cell. P_l stands for the contribution of the l -prototype. If the $\mathfrak{R}$ fragments are also attached, the combinatorial factors are the same as before and the final result after the summation up to an infinite number of $\mathfrak{R}$ fragments is

$$P_2 \times (1 - \mathfrak{R}\gamma^2 n^2)[1 + \frac{8}{3}\pi n\gamma(1 - \mathfrak{R}\gamma^2 n^2)]^{-1} \quad (l = 2) \quad (156)$$

$$P_1 \times [1 + \frac{8}{3}\pi n\gamma(1 - \mathfrak{R}\gamma^2 n^2)]^{-1} \quad (l = 4, 6, 8, \dots) \quad (157)$$

Let us recall that the static dielectric constant at low external fields, ϵ_0 , is given to the same approximation by the van Vleck expression (116), so that our result becomes

$$\lambda_2 \simeq P_2 \times (4\pi n\gamma)^{-1}(1 - \epsilon_0^{-1}) \quad (158)$$

$$\lambda_l \simeq P_l \cdot B^l; \quad B = (\epsilon_0 + 2)/3\epsilon_0 \quad (l = 4, 6, 8, \dots) \quad (159)$$

The contribution of the prototypes P_l of families $C_l^{(1)}$ can be successively calculated from the definitions of the Thiele semi-invariants λ_l in terms of the moments. Remembering that for our case

$$\lambda_l = B^l P_l$$

$$P_l = \sum_{i=1}^N p_l^{(i)}(m_1, \dots, m_l) \quad (160)$$

$$m_k = (\mathbf{s}_{\alpha i} m_i)^k = \begin{cases} (q\mu r_{\alpha i}^{-2})^k (k+1)^{-1} & k \text{ even} \\ 0 & k \text{ odd} \end{cases}$$

then

$$\lambda_l = (Bq_{\alpha i}\mu)^l (\sum_i r_{\alpha i}^{-2l}) \lambda'_l \left(0, \frac{1}{3}, \dots, \frac{1}{k+1}, \dots, \frac{1}{l+1}\right) \quad (161)$$

where $\lambda'_l(\dots)$ is the same polynomial as defined by Eq. (44).

The final result for the first three terms is

$$\begin{aligned} \beta w_1^{(\alpha)} = & -\frac{1}{2}\Gamma_a \left(1 - \frac{1}{\epsilon_0}\right) \frac{S_0}{4\pi} + \frac{1}{20} \Gamma_a^2 (n\gamma)^2 B^4 S_1 \\ & - \frac{1}{105} \Gamma_a^3 (n\gamma)^3 B^6 S_2 + \dots \end{aligned} \quad (162)$$

where

$$S_k = (\gamma')^{-k-1} \sum_{i=1}^N (r_{\alpha i}/a)^{-4-4k} \quad k = 0, 1, 2, \dots \quad (163)$$

and γ' is the geometrical factor relating the number density to a :

$$n = N/V = v^{-1} = (\gamma'_a)^{-1} \quad (164)$$

For an ion placed on a lattice site, and thus of radius about equal to that of the solvent molecules, the sums are well known; for a simple cubic lattice $\gamma' = 1$, $S_0 = 16.53$, and S_k decreases down to 6; for a face-centred cubic lattice $S_0 = 17.9$ and S_k decreases down to $12(\sqrt{2})^{-k-1}$.

The summation of the $C_i^{(1)}$ families up to an infinite order in q_α has been performed²² with the result

$$-\beta w_1^{(\alpha)} = W_B + W_S \quad (165)$$

where the Born-like term W_B is

$$W_B = \frac{1}{2} \Gamma_a (1 - \epsilon_0^{-1}) (S_0/4\pi) \quad (166)$$

and the dielectric saturation term in this approximation, W_S , is

$$W_S = \sum_{i=1}^N \left[\ln \left(\frac{\sinh y_i}{y_i} \right) - \frac{1}{6} y_i^2 \right] \quad (167)$$

Here

$$y_i = A_{\text{eff}} r_{zi}^{-2} = A_{\text{eff}}^* (r_{\alpha i}/a)^{-2}; \quad A_{\text{eff}}^* = A_{\text{eff}} a^{-2} = \beta q \mu a^{-2} B \quad (168)$$

It is interesting to note that the contributions of the prototypes P_i alone represent the direct interaction of the ion with solvent dipoles; when disregarding dipole-dipole interactions, i.e., when putting

$$\begin{aligned} U(0) &= U_{\text{sh}}^0(\mathbf{r}^N) \\ U_{\text{ch}} &= \sum_i u_{\alpha i} = \sum_i q_\alpha \mu r_{i\alpha}^{-2} \cos \theta_i \\ P(0) &= \prod_{i=1}^N \delta(\mathbf{r}_i - \mathbf{r}_{0i}) (4\pi)^{-N} \quad (\text{rigid lattice}) \end{aligned}$$

into

$$\exp [-\beta w_1^{(\alpha)}] = \int \exp [-\beta U_{\text{ch}}] P(0) d\mathbf{r}^N d\boldsymbol{\omega}^N$$

we obtain

$$\begin{aligned} -\beta w_1^{(\alpha)} &= \ln \prod_{i=1}^N \left\{ (4\pi)^{-1} \int \int d\boldsymbol{\omega}_i \exp [-y'_i \cos \theta_i] \right\} \\ &= \sum_{i=1}^N \ln \left(\frac{\sinh y'_i}{y'_i} \right) \end{aligned} \quad (169)$$

where

$$y'_i = A^\star (r_{\alpha i}/a)^{-2}; \quad A^\star = Aa^{-2} = \beta q \mu a^{-2}$$

Therefore our approximation for W_S may be called the single-dipole approximation. The direct ion-dipole interaction is modified owing to the presence of other molecules and this is approximately represented by the reduction factor $B = (\epsilon_0 + 2)/3\epsilon_0$, varying between 1 and $\frac{1}{3}$. This factor represents the long-range effect of independent simple chains connecting the dipole to the ion (see Table V).

Similarly, we can consider two dipoles, interacting with the ion and with each other through independent simple chains; this would be the case for families with two knotted points. An explicit calculation for the $C_4^{(2)}$ family has been made;²² its contribution, although much smaller than that of $C_1^{(1)}$, can be non-negligible.

It is interesting to note that $w_1^{(\alpha)}/kT$, as well as the first Born-like term, can be expressed in our approximation as a function of a single parameter, $A_{\text{eff}}^\star$. Unfortunately, it contains four independent parameters.

In Table I we give a sample of the results obtained for an ion placed on a lattice site of a simple cubic lattice or face-centred cubic lattice, whose radius is about equal to that of the solvent molecules, i.e., half of the lattice distance a . The contribution of higher powers of the ionic charge, W_S , was estimated graphically from a plot of calculated W_S for assumed values of $A_{\text{eff}}^\star$ between 1 and 12. Obviously W_S is of opposite sign to W_B .

The numerical values obtained depend strongly on the assumed spatial distribution of solvent molecules around the ion; e.g., all lattice sums are markedly increased if the ion is supposed to be placed in an interstitial position.

No experimental data are available for solutions of salts in non-polar or slightly polar solvents. It can be concluded, however, from rather too low values of $w_1^{(\alpha)}$, that the contribution of higher electric moments of the molecules is rather important and cannot be neglected, and we have shown that the use of the Born equations corresponds to only charge-dipole terms being taken into account. This supports the kind of approach used by Buckingham,²³ who took into account the ion-quadrupole

TABLE I. Calculated Free Energies of Solvation of Mono-, Di-, and Trivalent ($Z = 1, 2, 3$) Ions of Radii Equal to Those of Solvent Molecules, placed on a Lattice Site of a Simple Cubic (SCL) and Face-Centred Cubic (FCCL) Lattice. Units of kT at $T = 300^\circ\text{K}$

μ , Debye	q, A	$1 - \epsilon^{-1}$	B	A_{eff}^*	$W_B + W_s$			Lattice
					$Z = 1$	$Z = 2$	$Z = 3$	
0.5	3.00	0.542	0.639	4.117	66.2-6.3	264.7-46	595.6-140	SCL
		0.639	0.574	3.70	84.5-7.5	338-60	760.5-140	FCCL
0.5	5.00	0.172	0.885	2.05 ₃	12.6-0.5	50.5-6.5	113.6-21	SCL
		0.239	0.841	1.95	19.0-1.0	75.8-9.5	170.6-34	FCCL
1.0	5.00	0.502	0.665	3.09	36.8-2.2	137.2-21.5	331.2-59	SCL
		0.597	0.602	2.79	47.4-3.0	189.6-27.7	426.6-95	FCCL
1.0	6.00	0.348	0.768	2.47	21.2 ₅ -1.4	85.0-11.2	191.3-36	SCL
		0.448	0.701	2.26	29.7-1.6	118.8-15	267.3-45	FCCL
1.5	6.00	0.573	0.618	2.98	35.0-2.1	140.0-19.5	315.0-63	SCL
		0.661	0.559	2.70	43.8-2.5	175.1-25.3	393.9-74	FCCL
1.75	6.00	0.641	0.573	3.23	39.1-2.7	156.6-22.5	352.3-65	SCL
		—	—	—	—	—	—	FCCL

contribution in calculating the free energy of hydration of monoatomic ions.

The author wishes to express his thanks to Professor Prigogine and Dr Bellemans for suggesting the problem and to Dr Bellemans for numerous helpful discussions.

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MELTING MECHANISMS OF CRYSTALS

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I. MELTING AND CRYSTAL STRUCTURE

Structural information about melting processes is growing quite rapidly in bulk and in its significance for the chemical physics of condensed states of matter. General statistical considerations about the numbers of ways of constructing the solid phase W_S and the liquid phase W_L and the application of the Boltzmann expression

$$S_f = R \ln (W_L/W_S)$$

to the entropy of fusion, S_f , indicates the usefulness of classifying melting processes in relation to the various types of structural disorder that can be envisaged in different types of crystal lattices. Such a classification is particularly appropriate when the melts can be described (in terms of statistical thermodynamic models) as *quasi-crystalline*. When such an approximation is adequate, the enumeration of the number of independent ways of

realizing the liquid state near the freezing point mainly involves a consideration of the types of disorder that can also be encountered in the solid state. For other systems in which the melts depart markedly from a quasi-crystalline behaviour, the classification of the types of disorder introduced on melting must be more diversified. However, a systematic structural description of these types still provides a very useful basis for statistical theories of melting.

Structural considerations of melting processes also suggest a number of general questions about melting. Not all these questions can be examined in detail in the present article, but the main headings are summarized in what follows.

II. PREMELTING AND PREFREEZING PHENOMENA

Classical thermodynamics regarded melting as the outcome of the intersection of free-energy surfaces of a solid (subscript S) or a liquid (subscript L)

$$G_S = f_S(p, T) \quad \text{and} \quad G_L = f_L(p, T)$$

yielding a curve relating melting temperatures and pressures. In all other respects these two surfaces were regarded as referring to two wholly independent phases. Premelting phenomena in crystals or prefreezing in the melts as the melting point is approached have no basis if the solid and liquid phases really are independent, as in the classical formulation of phase equilibria. Statistical thermodynamics would, on the other hand, anticipate some premelting in practically all crystals, in so far as those structural types of disorder which become very prominent on passing from crystal to melt can usually be accommodated in small concentrations in the crystal below the freezing point. In modern descriptions of melting the question to be decided is not whether there is any premelting, but whether defect formation becomes really appreciable below the melting point. The answer depends on the experimental techniques used to evaluate the presence of defects in thermal equilibrium in the crystals.

Examples of premelting have sometimes been suspect, because impurities soluble in the melt but insoluble in the crystals lead to the formation of small amounts of the actual liquid phase at

temperatures T below the melting point, T_f^0 , of the ideal pure crystals. Various criteria can, however, be applied to verify that the observed premonitory changes refer to the crystalline phase, regardless of liquid formation. In principle, any property P_r of the solid may be examined, including thermodynamic parameters such as the volume, the heat content, and their derivatives, and non-thermodynamic parameters such as the electrical and thermal conductivities, dielectric and other relaxation times, or intensities of X-ray reflections. The anomalous change ΔP_r is estimated at any temperature in the premelting region below T_f^0 by subtracting the "normal" value for the solid at the same temperature, as estimated by extrapolation from low temperatures. When premelting is very marked, as in the silver halides (cf. Reference 28), this is apparent even from direct plots of ΔP_r against $(T_f^0 - T)$. When smaller anomalies are under examination, as for KCNS^{20,22} or for the alkali metals,⁴ it is sometimes helpful to discriminate between trivial phenomena due to liquid formation and those due to accelerated defect formation in the crystals as the melting point is approached, by examining the trend of the functions $1/\Delta P_r$ plotted against T and $\log \Delta P_r$ plotted against $1/T$.

When any likely impurities in the system readily form solid solutions in the crystals, they may be very difficult to remove by conventional methods. Effects of such foreign molecules in the crystal lattice can profoundly modify barriers to molecular rotation, and can thereby enhance premelting. In favourable cases, this can be tested by the direct addition of the appropriate impurity, whose structure must be so close to that of the primary molecules that the foreign species can easily be accommodated in the crystals. Some experimental examples have been investigated by Ubbelohde,²⁵ Oldham and Ubbelohde,¹⁸ and Thompson and Ubbelohde²⁴ (cf. Reference 27).

Prefreezing phenomena are less easily summarized than premelting ones partly because they are more diversified and partly because they have been less well characterized up to now. In quasi-crystalline melts, minute concentrations of "crystalline" regions can be inferred on the basis of observations on spontaneous nucleation at the critical supercooling temperatures T_c , which for many quasi-crystalline melts show a constant ratio to the

freezing points T_f . Melts of quasi-crystalline structure may be expected to follow the empirical rule³

$$T_c/T_f \approx 0.8$$

However, other melts are now being studied, and are likely to be quite numerous, for which quasi-crystalline models are far from adequate. In such cases, on approaching and traversing T_f the (supercooled) melt behaves as if it contained an increasing proportion of "clusters" whose packing energy relative to the less organized regions in the liquid is close to that of minute crystalline regions. These melts are more fully discussed below.

III. SIMILITUDE RULES FOR MELTING

The enormous variety of known atoms and molecules is much greater than the variety of crystal lattices in which they are found to crystallize. Structural descriptions of melting suggest the possibility that crystals with similar lattices may melt to give liquids with similar disorder, so that the entropy of fusion and other structural parameters might be the same for all atoms or molecules of the same crystal type. However, examination of known data shows that similitude rules have only a limited applicability, no doubt partly because in many crystals conflicting contributions to melting are made by various mechanisms for introducing disorder. Even salts whose ions have an inert gas structure fail to show accurate similitude in entropies of fusion. This is illustrated in Tables I, II, IIIa, and IIIb. One difficulty is that melting seldom appears to involve any principle of corresponding states, unlike the transition from a liquid to a gas. Attempts to find rules of similitude from the standpoint of entropy-disorder increases, or on a purely geometrical basis, usually start from intuitive thinking rather than from well developed statistical models. Thermally dimensionless quantities, for example $(C_L - C_S)/S_f$ or $(\alpha_L - \alpha_S)T_f$, where C_L is the specific heat of the liquid and C_S of the solid, and α is the corresponding volume expansion coefficient, might at first sight seem to offer hopeful correlations for large numbers of crystals. Insufficient information is available to test this suggestion adequately. However, a more detailed consideration of melting discussed below

shows that several mechanisms may contribute; when more than one kind of structural disorder is important for a crystal changing to a melt the search for simple similitude rules seems particularly unprofitable.

IV. CRITICAL MELTING

By analogy with critical conditions for the transition between liquids and gases, there has been considerable discussion about the possibility of critical conditions for the transition between solids and liquids at sufficiently high temperatures and pressures.^{7,11} Most of these discussions have dealt with crystals of extremely simple structure, such as those of the inert gases, and have thus failed to recognize that increase of pressure and temperature can affect different mechanisms of disorder very differently. In the experiments so far reported no critical conditions for very simple crystals have even been approached. Chances of success may, however, be much greater for crystals for which several mechanisms of disordering, such as those discussed below, contribute to the melting process.

V. SOME PROMINENT MECHANISMS OF MELTING

In the general structural sequence, for increasing disorder,

Ideal crystal $\rightarrow$ crystal with thermal defects $\rightarrow$

$$\left\{ \begin{array}{l} \text{quasi-crystalline melt} \rightarrow \text{melt with} \\ \text{non-crystallizable structures} \end{array} \right\},$$

some of the more prominent sources of increase in entropy on passing from crystal to melt can be briefly summarized as follows.

A. Positional Disorder

Crystals of the inert gases can develop only positional defects with respect to the ideal crystal lattice. Well known types of defects include lattice vacancies (Schottky defects) and the occupation of interstitial lattice sites (Frenkel defects). As long as the concentration of such defects remains small, as is the case in most well known crystals, their energy of formation can be regarded as independent of the neighbouring sites. But when the

concentration becomes large, on passing from crystal to quasi-crystalline melt, the work ε of defect creation depends on the proportion of defect sites already present. Statistical theories of simple positional melting have been put forward for crystals of the inert gases.¹¹ Co-operative positional defects (dislocations) can also be envisaged,¹⁸ but no satisfactory theory of melting has yet been put forward on this basis for inert gas atoms.

According to evidence from X-ray studies, increases in positional disorder occur for the melting of all known types of crystals. Except for the very few crystal lattices for which the number of nearest neighbours is small (C.N. 4 or less), this increase in positional disorder is accompanied by an increase in volume on melting at constant pressure. For the inert gases the increase in volume is about 15%. This is explained by the consideration that with co-ordination numbers (C.N.) higher than 4, large repulsion energies will be introduced by positional defects unless the crystal volume is allowed to expand to allow for their presence. For testing theories of melting, the number of inert gases is unfortunately very small. In view of the extremely widespread occurrence of positional disorder on melting, attempts have been made to extend simple structural models for this melting process

TABLE I. Entropies of Fusion that Involve
Predominantly Positional Disordering

Substance	S_f , cal/mole/°C
Ne	3.26
Ar	3.35
Kr	3.36
Xe	3.4
Camphor	3.6
Camphorquinone	3.4
Bornylamine	3.3
Camphene	2.8
α -cis-3,6-Endomethylene ¹⁹ Δ^4 -tetrahydrophthalic acid anhydride	2.67
cis-3,6-Endoethylene ¹⁹ hexahydrophthalic anhydride	3.21
Di-lactone of 4,5-dioxy ¹⁹ 3,6-endoethylene hexahydro- phthalic acid	3.1

for the inert gases to a variety of other crystal types, with spherically symmetrical units. This appears to be fairly successful for molecular crystals of those "globular" organic molecules whose repulsion envelopes are roughly spherical and which form no primary vacancy bonds between neighbours, as is shown by the examples collected in Table I.

However, even close-packed crystals of metal atoms do not

TABLE II. Entropies of Fusion of Some Metals

Substance	S_f , cal/mole deg ⁻¹
Alkali metals	1.5-1.7
Cu, Ag, Au	2.2-2.3
Zn, Cd, Hg	2.5-2.6
Al	2.7
Ti	1.8
Fe	2.0
Ni	2.45

have entropies of fusion in accord with the similitude rules for crystals of the inert gases, as is shown by Table II.

One possible explanation is that co-operative defects may make a large contribution to positional melting in metal crystals, as has been suggested in a theoretical model.¹⁷ Another explanation is that molten metals may contain clusters of atoms, particularly near their melting point. Prefreezing phenomena in metals¹⁵ give some support to this suggestion, but more experimental work seems desirable to test how far they occur.

Crystals containing ions with an inert gas structure constitute another type of lattice which at one time was thought to show predominantly positional melting. However, the entropies and volume changes on melting such crystals, recorded in Table III (cf. Reference 23), do not support any simple generalized model for positional disordering. As already stated, similitude rules derived for the inert gases clearly do not apply. Since the crystals are geometrically broadly comparable, discrepancies in structure must be looked for mainly in the melts.

Complicating factors that lead to discrepancies from the similitude rules are probably due to local polarization accompanied

by ion-pair formation in the melt. Anion-anion repulsions also become more prominent as the radius ratio r_-/r_+ in these ionic melts increases. When the ions depart from the inert gas structure, because they belong to B groups in the periodic system, or

TABLE III

(a) Entropies of Fusion (cal/g.ion deg⁻¹) of Salts with Ions of Inert Gas Structure

Cation \ Anion	F	Cl	Br	I
Li	5.78	5.6	~4.9	—
Na	5.5	6.7	6.0	5.6
K	5.8	6.2	4.9	4.3
Rb	—	4.4	3.9	—
Cs	—	3.9	—	—

(b) Volume Changes ($\Delta V_f/V_s\%$) on Fusion of Salts with Ions of Inert Gas Structure

Cation \ Anion	F	Cl	Br	I
Li	29.4	26.2	24.3	—
Na	27.4	25.0	22.4	18.6
K	17.2	17.3	16.6	15.9
Rb	—	14.3	13.5	—
Cs	—	10.5	—	—

because they are polyatomic and thus non-spherical, melting often appears to lead to the formation of association complexes.

B. Rotational Disorder

Crystals containing polyatomic units of structure which are effectively non-spherical usually exhibit some increase in disorder in the mutual orientation of these units when the crystal melts. For such crystal lattices, the total entropy of fusion, S_f , may be written as the sum of two terms: $S_f = S_{\text{pos.}} + S_{\text{or.}}$.

Techniques for increasingly detailed study of the mutual orientation of molecular axes in such crystals and in their melts have revealed a wide diversity of behaviour with respect to the term $S_{or.}$, even for molecules which show a formal similarity of structure. One reason is that potential barriers opposing the randomization of orientation of molecular axes are very sensitive to details of molecular conformation. One extreme is presented by crystals which have λ -transitions in the solid state. Considerable and in some cases complete randomization of mutual orientation of molecular axes is found to occur above such lambda points. As a result, such crystals are already considerably disordered rotationally below the melting point. Approximately, it then follows that on melting only positional disordering increases sharply and $S_f = S_{pos.}$ as for spherical units of structure.²⁶ When the barriers opposing randomization are too great to permit lambda transitions below the melting point, the expansion in volume on melting often lowers these barriers to such an extent that each molecule can be regarded as quasi-spherical in the melt. In the equation $S_f = S_{pos.} + S_{or.}$ the second term then assumes a limiting value for complete rotational disorder. Examples of each type of behaviour for simple polyatomic molecules are given in Reference 26. However, when the departure from the spherical shape of the molecules becomes very marked there is insufficient room to permit complete randomization of molecular orientation even in the melt. Systematic studies for a number of rigid aromatic molecules^{1,2} suggest that such a behaviour may be fairly common. An extreme case is presented by liquid crystals, in which rotation about at least one of the principal molecular axes is practically inhibited below the clearing point.

VI. MELTS FOR WHICH QUASI-CRYSTALLINE MODELS ARE INADEQUATE

Increases in configurational disorder on melting are particularly prominent with flexible molecules, such as the homologues of long-chain aliphatic compounds with the general formula $C_nH_{2n+1}X$, where X is an end-group such as H, I, COOH, etc. The crystal lattice normally selects only one out of a number of configurations, usually the one which is fully stretched, and packs

it in a regular three-dimensional assembly with minimum potential energy. Figure 1 illustrates (cf. Reference 29) a few out of the many configurations for $n\text{-C}_{12}\text{H}_{26}$. On melting, each of the various crumpled configurations can be formed with approximately

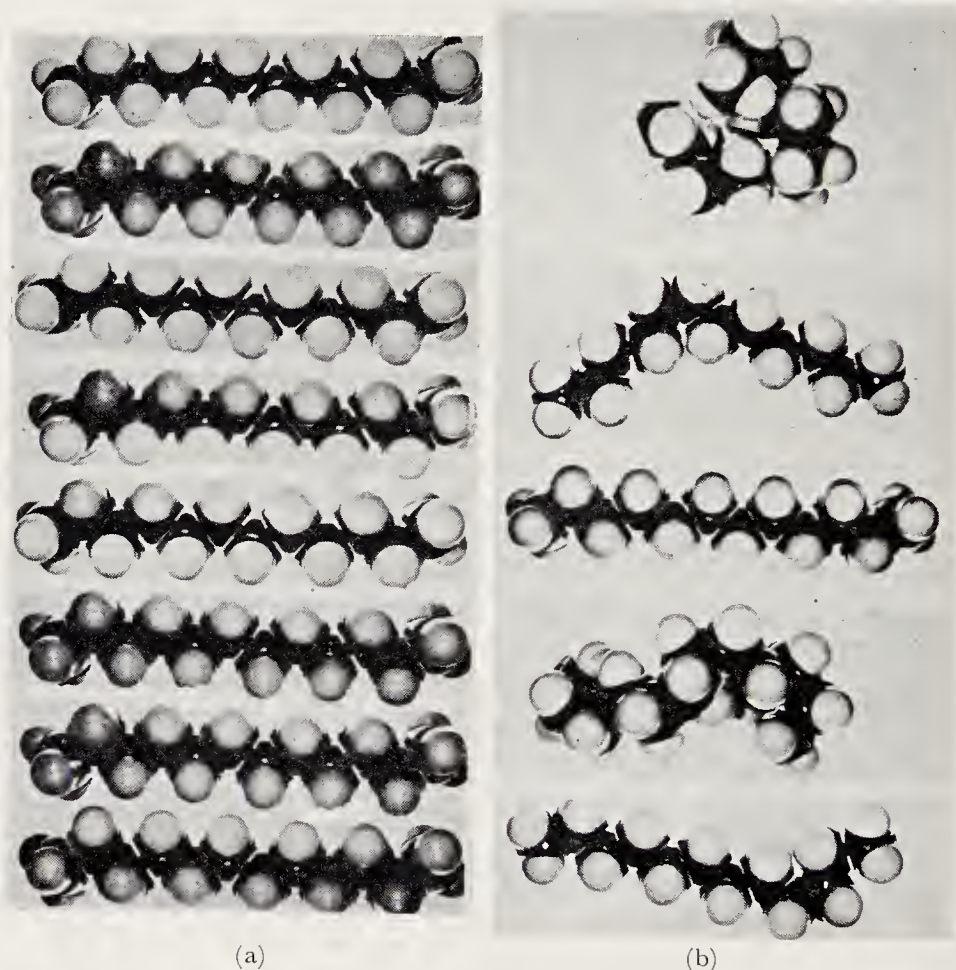


Fig. 1. (a) n -Dodecane molecules in the crystals; (b) some of the configurations of n -dodecane in liquid or gas.

equal potential energy (cf. Reference 12). This introduces an additional mechanism of disorder. In the composite melting process that operates for such crystals,

$$S_f = S_{\text{pos.}} + S_{\text{or.}} + S_{\text{config.}}$$

For large values of n , the increase in the configurational entropy $S_{\text{config.}}$ can swamp the other two modes of increasing disorder.

This leads to an asymptotic limiting melting point in each homologous series, as has been discussed more fully elsewhere.²⁶ Evidence for the existence of a range of crumpled configurations in melts of flexible molecules can be derived from various thermodynamic parameters.

As has already been indicated, one way of arriving at the quasi-crystalline melt is to expand the crystal and to introduce the appropriate positional and orientational defects in the expanded crystal lattice. The total volume increase on melting, ΔV_f , is calculated in two stages, allowing first for the increased separation of the points of the reference lattice, followed by the increase in volume due to the additional defects introduced to create the disordered melts. But melts which contain a variety of configurational isomers of flexible molecules obviously do not conform even approximately to quasi-crystalline models of the melt. A melting mechanism such as the creation of configurational disorder may not be foreshadowed to any appreciable extent by corresponding thermal defects formed in the crystal below the melting point. This has interesting implications for various theories about liquid mixtures (solutions) containing flexible molecules, since if the term $S_{\text{config.}}$ is appreciable on melting, it may also undergo appreciable changes on admixture of a second liquid with the melt. Abnormal entropies of mixing will ensue.

VII. FORMATION OF ASSOCIATION COMPLEXES ON MELTING

A second mechanism for increasing disorder on melting which cannot be conveniently represented by a quasi-crystalline model for the melt involves the formation of association complexes. Quite generally, these can be defined as clusters of the units of structure (e.g., molecules or ions) in the crystal which have approximately the same distance between nearest neighbours as in the crystal lattice, but which need not have the full regularity of crystal packing. As already stated, only one particular form of cluster, *the crystal nucleus*,* can normally be extended indefinitely

* Any polymorphs of about the same free energy as the most stable crystal form would be represented in the melt by the thermodynamically determined concentrations of crystal nuclei of types characteristic of their specific structures.

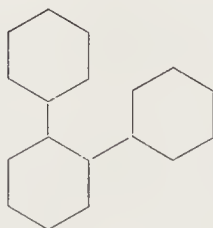
by the progressive addition of more and more units of structure, in three dimensions. Crystal packing completely fills space, in a regular way, whereas extending the growth of any other less ordered cluster requires the incorporation of dendrites, fronds, and voids. If the concentration becomes appreciable, cluster formation in melts can often be detected from changes in the transport properties as the melt approaches and is supercooled below the freezing point. For example, normal quasi-crystalline melts follow an Arrhenius equation in the dependence of their viscosity on temperature, so that a straight line in conformity with the η equation, $\log \eta = A + B/T$, is obtained on plotting experimental values.

An illustration is provided by the series of homologous liquids: benzene, biphenyl and *p*-terphenyl, which all show this behaviour, with appropriate changes of the transport parameters, as the molecular weight increases.²

TABLE IV. Viscosity Parameters for Linear Polyphenyl Melts, $\log \eta = A + E/RT$ near the Melting Point

Molecule	$A \times 10^3$	E , kcal/mole
Benzene	7.19	2.63
Biphenyl	5.43	3.80
<i>p</i> -Terphenyl	16.4	3.76

In marked contrast with this behaviour, branched polyphenyl molecules such as *o*-terphenyl



show a marked enhancement of viscosity above the Arrhenius value, as their temperature approaches T_f and falls below it. Some comparative plots are illustrated in Fig. 2, a, b, c. This anomalous

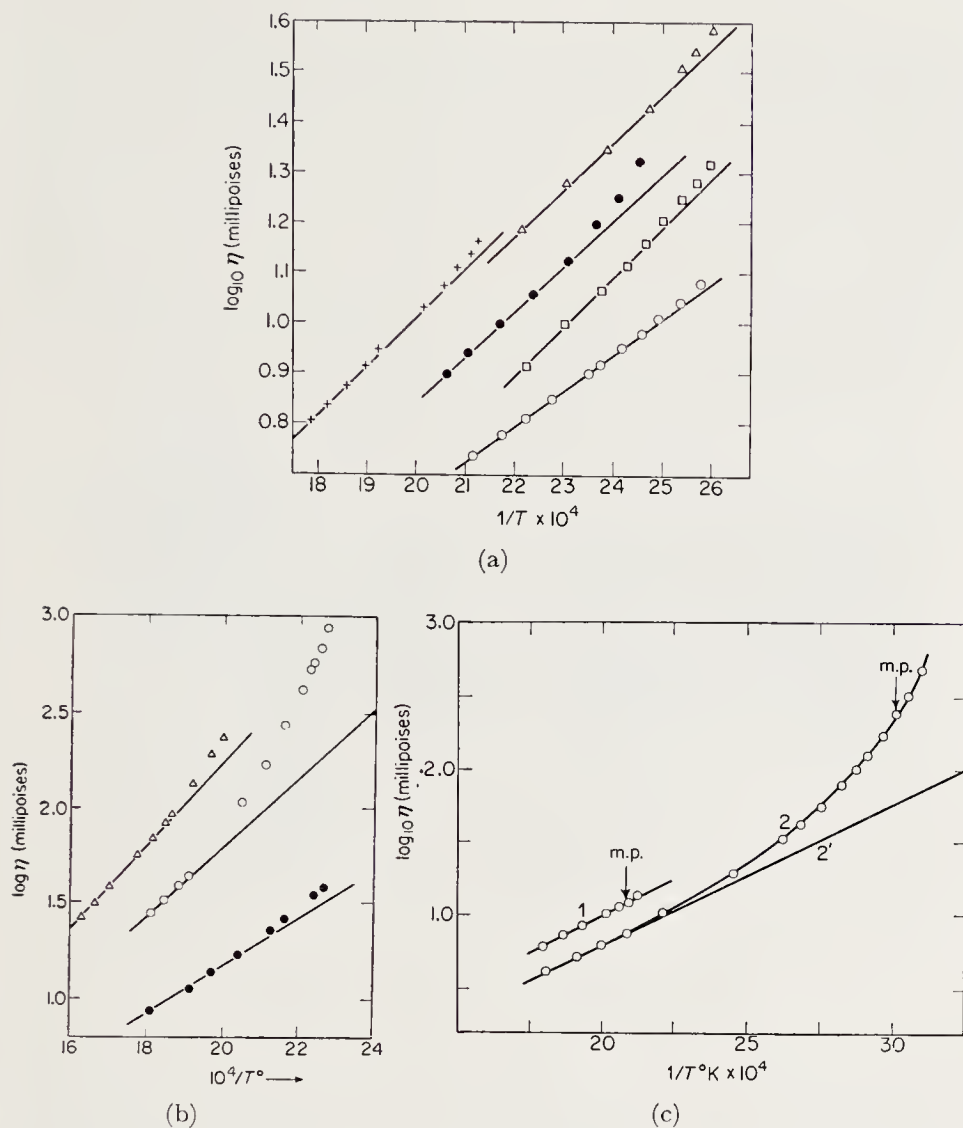


Fig. 2. (a) Plots of experimental results. Abscissae for triphenylene $+$ $+$ $+$, fluorene $\circ$ $\circ$ $\circ$ and fluoranthene $\triangle$ $\triangle$ $\triangle$ are as shown. The abscissa for pyrene $\square$ $\square$ $\square$ is shifted 2.5 units, and for 1,2-benzanthracene $\bullet$ $\bullet$ $\bullet$ 1.5 units to the right. (From McLaughlin and Ubbelohde.¹³) (b) Plots of $\log_{10} \eta$ against $1/T$ ($^{\circ}\text{K}$). $\bullet$ $\bullet$, 1,3,5-triphenylbenzene; $\triangle$ $\triangle$ tri-*p*-diphenylbenzene; $\circ$ $\circ$, 1,3,5-tri- α -naphthylbenzene; abscissa shifted one unit to the right. (From Magill and Ubbelohde.¹⁶) (c) Curve 1, viscosity of triphenylene; curve 2, viscosity of *o*-terphenyl; curve 2', extrapolated low temperature viscosity of *o*-terphenyl. Arrows indicate melting points of each species. (From McLaughlin and Ubbelohde.¹⁴)

increase in viscosity has been attributed to the formation of an increasing proportion of clusters which are compelled to move as a whole in the fluid because the molecules in them are linked or interlocked together in some way. Such a model can be examined in the light of a theory first developed by Einstein to describe the enhanced viscosity η_i of colloidal solutions. If a volume fraction ϕ of the liquid consists of regions that move together like colloidal particles, the actual viscosity η_i will be enhanced relative to that of the hypothetical supporting monomolecular fluid η according to the equation (for spherical particles)

$$\eta_i/\eta = 1 + 2.5\phi + 7\phi^2$$

which applies approximately provided ϕ does not exceed about 0.3. On the basis of this hypothesis, the volume fraction of clusters

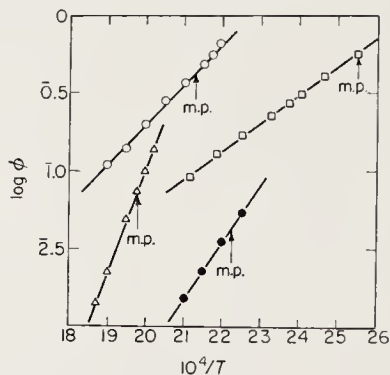


Fig. 3. Volume fraction of clusters in melts of phenyl benzenes. (From Magill and Ubbelohde.¹⁶)

present near the freezing point in melts of various terphenyls can be readily determined, and follows the temperature dependence illustrated in Fig. 3. This method of determination only evaluates the fraction ϕ for the whole melt and does not yield the number of molecules, n , linked together in each cluster. At present n can only be determined from this kind of prefreezing phenomenon in melts by indirect and probably not very reliable means (see, e.g., Reference 15).

All that is necessary to produce anomalous transport properties near the freezing point of a melt is some mechanism of interlocking or association that causes the molecules in a cluster to move as a whole during intervals of time that are long compared with the

time interval characteristic of the relaxation process which determines the property being considered. It should be stressed that in examples that give apparently similar non-linear plots of viscosity as a function of temperature, the origin of the forces of association may be very different. For the polyphenyls referred to above, probably Van der Waals' forces similar to those that determine the crystal formation also operate in cluster formation.

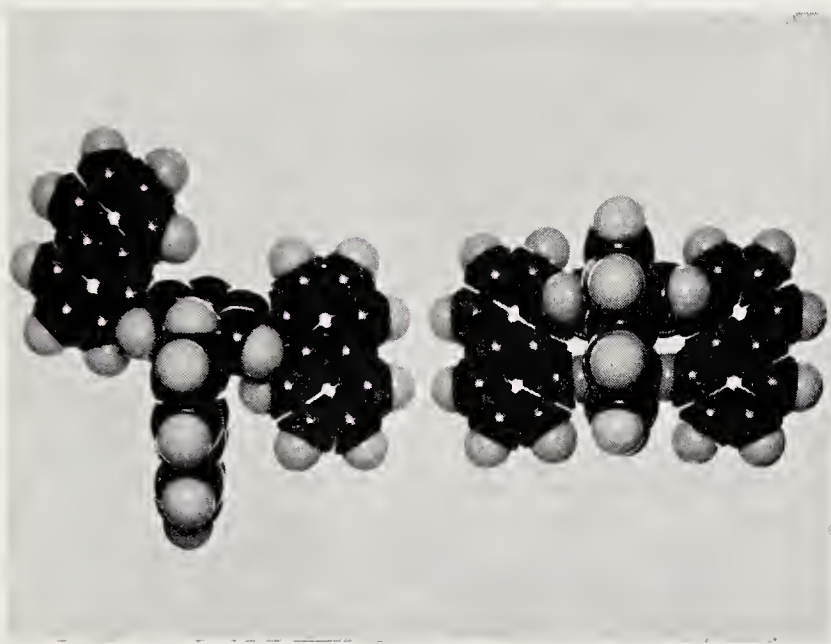
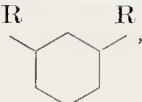
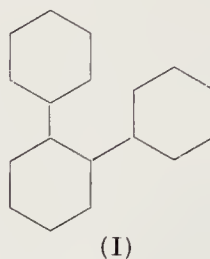
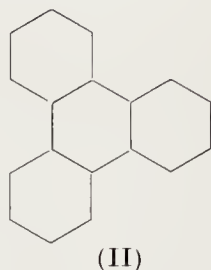


Fig. 4. Two forms of tri- α -naphthyl benzene ,

which shows marked interlocking in its melts.

Molecular shape is an important factor in determining non-crystallizable association of molecules; thus, clusters become prominent in these aromatic molecules, particularly for structures such as *o*-terphenyl with marked re-entrant surfaces that favour close-packing of a few units into more or less irregular assemblies. Molecules with a strong tendency to form non-crystallizable clusters also readily give supercooled melts and pass into glasses much more easily than their analogues in which cluster formation is less prominent.¹⁶ With respect to properties such as the dependence of molecular volume on temperature, a good example is

presented by the molecule 1,3,5-tri- α -naphthyl benzene (cf. Fig. 4). Melts of this substance readily supercool and eventually pass into a glass which shows thermodynamic properties similar to those of glycerol glasses. Some additional evidence is provided by the marked contrast in prefreezing behaviour (Fig. 2c) between the closely similar molecules *o*-terphenyl (I) and triphenylene (II).¹⁴



Unlike I, II shows practically no clustering, in conformity with its much less pronounced re-entrant surfaces.

For other melts other forces of association may lead to cluster formation; the average size of a cluster may also be different. In the limit, very small clusters in ionic systems are best described as "association complexes". Examples of such complexes have long been known in analytical chemistry as complex ions.

VIII. ASSOCIATION COMPLEXES IN IONIC MELTS

Thermodynamic and structural evidence points to the marked departure from spherical symmetry of polyatomic ions as one factor which strongly favours the formation of association complexes when the crystals are melted. General indications may be

TABLE V. Melting Points of Some Salts with Polyatomic Anions in °C (Halides are Given for Comparison)

Anion Cation	Cl	I	OH	NH ₂	ClO ₃	ClO ₄	NO ₃	CH ₃ COO ⁻
Li	613	440	450	374	127	236	255	—
Na	801	651	318	210	255	482d.	307	324
K	776	723	360	335	368	610	334	292
Rb	715	642	300	—	—	—	310	246
Cs	646	621	272	—	—	—	414	194

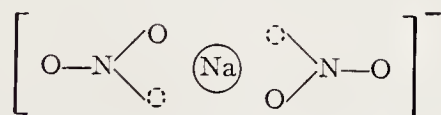
derived from a survey of the melting points of salts containing polyatomic anions.⁶ Values are recorded in Table V.

Salts whose anions have particularly asymmetric shapes, such as nitrates, can show surprisingly low melting points and abnormally small increases in volume on passing from crystal to melt, as is exemplified in Table VI. This tendency to favour the liquid

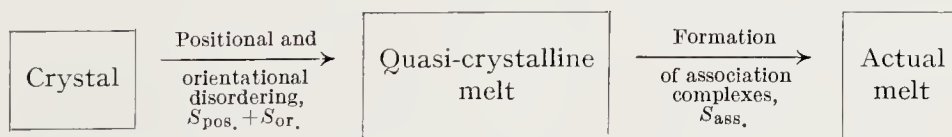
TABLE VI. Volume Changes ($\Delta V_f/V_s\%$) on Fusion of Salts with Polyatomic Anions

	NO ₃	SCN	ClO ₃	HSO ₄
Li	21.4	—	—	—
Na	10.7	7	—	—
K	3.32	10	10	4
Rb	—0.23	—	—	—
Cs	12.1	—	—	—
Ag	0.7	—	—	—

state at unusually low temperatures has been explained on the general hypothesis that the melts of such salts contain significant concentrations of association complexes, possibly such as the tetrahedral co-ordination complex:



Appreciable concentrations of such complexes may be expected to modify melting parameters in a number of ways, as can be seen when the formation of the melts is broken up into the hypothetical sequence:



The total entropy of fusion to form the actual melt, $S_{\text{pos.}} + S_{\text{or.}} + S_{\text{ass.}}$, can be obtained for lower values of the total heat of fusion, H_f , made up of the corresponding enthalpy terms $H_f = H_{\text{pos.}}$

$+ H_{\text{or.}} + H_{\text{ass.}}$, than is possible when association complexes do not contribute. This is because the third term in H_f is small or even negative. As a consequence, the ratio $T_f = H_f/S_f$ tends to be lower for such melts than for those in which association is unimportant. A similar argument applies to the total volume increase on melting, regarded as split up into the hypothetical sequence of operations:

$$\Delta V_f = \Delta V_{\text{pos.}} + \Delta V_{\text{or.}} + \Delta V_{\text{ass.}}$$

ΔV_f tends to be lower than for melts of inert-gas-type ions because the third term is likely to be negative, since ions in the complexes actually pack more closely than the average volume occupancy for the melt as a whole.

IX. A CONGLOMERATE MODEL FOR IONIC MELTS

This model of a melt containing association complexes implies the presence of regions for which a quasi-crystalline description referred to an expanded crystal lattice is still appropriate, mixed with voids and with regions that consist predominantly of association complexes or clusters whose packings are "non-crystallizable". Provided the concentration of non-crystallizable packings does not become so high that the clusters interlock, this somewhat primitive mixture model can probably serve to describe the thermal and transport properties of such melts without too much distortion. A statistical model for computing thermodynamic and transport properties of liquids⁸ adopts a rather similar concept. Such liquids can in fact be regarded as consisting of a conglomerate of regions of different structure whose individual properties can be described in simpler terms. In this connection the relaxation time for the persistence of any particular cluster need not be specified, except that it must be long compared with the characteristic time of any particular transport property for clustering to influence that property. There is likewise no need to specify whether the lowered potential energy which causes a cluster to form arises from purely electrostatic forces or whether quantum-mechanical hybridization of orbitals leads to some covalent bonding in the complex.

Non-thermodynamic evidence supports the general assumption that salts with low melting points include ion association with their other melting mechanisms. For transport properties such as the viscosity,⁹ the evidence is only indirect. Direct evidence can be most readily obtained from studies of changes in the ultra-violet absorption spectra when ionic crystals melt.^{5,21,22} These spectra are particularly informative since the act of absorption of light corresponds to the transfer of an electron to an excited orbital whose radius r_0 is strongly influenced by the shell of the nearest neighbour cations. The absorption bands give information about the structure of the association complexes and of any "normal quasi-crystalline" regions of the melt, and disregard the role of any voids, which, however, play a large part in many other properties of ionic melts. They provide a means of examining the local structure around the ions largely independent of the usual longer-range contributions from next nearest and even more remote neighbours.

By making various simplifying assumptions it can be shown that the location of the peak absorption E_{max} can be related to the radius r_0 of the shell by an equation of the form

$$\frac{dE_{\text{max.}}}{dT} = -C \frac{dr_0}{dT}, \text{ where } C \text{ is a constant} \quad (1)$$

Equation (1) can be tested in the solid state by measuring absorption spectra at various temperatures. It is found that the peak shifts towards longer wavelengths as the temperature rises.

Despite the rather crude simplifying assumptions made, values calculated from measured shifts of $dE_{\text{max.}}/dT$ show reasonably good correlation with values of dr_0/dT calculated from the macroscopic thermal expansions of the crystals. This gives particular interest to the change Δr_0 observed in the absorption peaks on passing from crystal to melt. For a melt with simple ions of inert gas structure, such as lithium iodide, the change Δr_0 implies an increase in the average radius of the shell of nearest neighbours on melting. On the other hand, with melts for which other evidence indicates the presence of association complexes in marked concentration, the average radius contracts on melting.

For the alkali nitrates, shifts in the second absorption maxima, corresponding to changes in temperature, are well defined. Shifts to lower frequencies imply increases in ν_0 and are entered as positive.

TABLE VII. Shift (cm^{-1}) in Band Peak E_2

Substance	Solid from 20°C to 5° below M.P.	Solid from 5° below M.P. to melt 5° above it
NaNO_3	970	—180
KNO_3	380	— 60
RbNO_3	630	—320
CsNO_3	730	—180

This difference in behaviour of the shift of ultra-violet absorption on melting is borne out by other characteristics of the ultra-violet absorption bands. For melts that appear to contain association complexes, these bands tend to be narrower and may have absorption maxima of intensity comparable with that in the crystals. This contrasts with melts of ions with inert gas structures, but conforms with expectations for association complexes in which the packing, though of lower symmetry, is somewhat tighter than in the crystals.

X. SYMMETRY DECREASES ON MELTING

A final general comment may be added about the decrease in symmetry of the arrangement of nearest neighbours around any unit of structure when a crystal changes to a melt by undergoing positional disordering, together with orientational disordering in some cases. Decreased symmetry leads to decreased neutralization of the forces due to neighbouring units acting on any unit in the melt. Where strong ligand fields are absent, no further consequences may ensue and a quasi-crystalline melt results, but if the decreased neutralization of forces permits new local packings of molecules to develop, the melt departs from any simple quasi-crystalline model and becomes a conglomerate. Two types of non-crystallizable arrangements have already been referred to

above, with reference to flexible molecules and with reference to ionic melts in which there are association complexes. Other types arise when the crystals contain complex ions, such as $[\text{AlF}_6]^{3-}$ in cryolite. In such crystals, the symmetry of the electrostatic deformation forces due to the nearest neighbour cations largely neutralizes their perturbation of the complex anion, except perhaps on approaching the melting point if the concentration of vacancy defects becomes appreciable.¹⁰ But the positional and orientational disorder introduced on melting leads to much less symmetrical deforming forces and the highly charged polyatomic ion breaks up. There is evidence that the dissociation $[\text{AlF}_6]^{3-} \rightarrow [\text{AlF}_4]^- + 2\text{F}^-$ occurs to a considerable extent on melting. Other complex ions found in crystals may dissociate to give simpler complexes of lower electrostatic charge on melting for the same reason. The phenomenon of non-congruent melting can often be explained along these lines. Clearly such possibilities open wide vistas on the structure of ionic melts whose ions depart from the simple inert gas structure, and indicate the kind of statistical treatment which will eventually be successful in accounting for their thermodynamic behaviour.

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